1,2-Diaza-2,4,6,8-cyclooctatetraene

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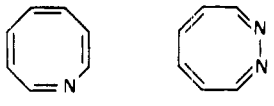
1,2-Diazocine is prepared from 7,8-diazatetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene by four methods that excite the precursor into its triplet state of lowest energy. The ^{1}H NMR spectrum shows its structure to be **2** and not **2a** and its conformation to be **12**. When heated it gives benzene and pyridine, and when irradiated with ultraviolet light it gives only benzene. Reasons are discussed why pyridine is formed in the one reaction and not in the other. The kinetics are recorded for the thermal reaction. Evidence that its double-bond and valence isomers are destabilized because lone pairs of electrons on adjacent nitrogens repel each other is sought in **2**'s reduction potential, but it cannot be recognized. Valence tautomers **7**–**11** are not detected in **2** by NMR spectroscopy.

The nitrogen analogues of cyclooctatetraene should share some of the parent's rich chemistry,[1] but they have not attracted much attention, no less scrutiny. The 2-alkoxyazocines are exceptions, for Paquette and his associates synthesized them and investigated them extensively,[1a,2] but the unsubstituted azocine (**1**), which Hedaya et al. prepared a number



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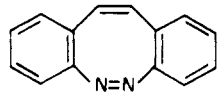

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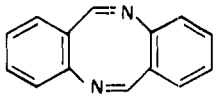

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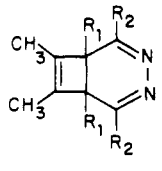


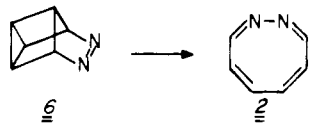
5

R_1	R_2
H	C_6H_5
CH_3	C_6H_5
CH_3	CH_3

of years ago from diazabasketene (by flash vacuum pyrolysis) and characterized in solution at low temperature, is extremely unstable, and it has not been looked at since.[3]

In contrast, 1,2-diazocine (**2**), called below DCOT (1,2-diazacycloocta-2,4,6,8-tetraene), turns out to be stable enough to isolate,[4,5] and this paper describes its synthesis, analyzes its structure, and presents some of the properties it exhibits when heated, photolyzed, and electrolyzed. Before DCOT was synthesized, dibenzo[*b*,*f*][1,2]diazocine (**3**)[6] and some substituted dibenzo[*d*,*f*][1,2]diazocines[7] had been prepared and found to be stable, and so incidentally had dibenzo[*b*,*f*]-[1,5]diazocine (**4**).[8] But experiments that might have yielded 1,2-diazocines free of benzo groups, in which molecules **5** had been pyrolyzed, failed to give stable eight-membered rings, for although these probably formed, under the conditions of their preparation they seemingly valence tautomerized and extruded nitrogen, giving substituted benzenes instead.[9] DCOT distinguishes itself from these molecules by not having a benzo group to prevent valence tautomerism to a structure like **5**; yet it does not tautomerize.

Synthesis. DCOT can be obtained (eq 1) from the polycyclic azoalkane **6**[5a,10] by four methods:[4,5] (i) irradiation at low



6 **2** (1)

(i) *hν*, −78 °C
(ii) *hν*, $C_6H_5COCH_3$
(iii) *hν*, $S_0 \rightarrow T_1$ (490 nm)
(iv) *hν*, 1400 psi O_2

temperature (−78 °C) with 366-nm light, which carries **6** into its first excited singlet state; (ii) excitation with photochemically excited acetophenone; (iii) excitation at room temperature with 490-nm light, which carries **6** straight into its lowest energy triplet state; and (iv) irradiation at ambient temperature with 366-nm light, but under 1400 psi pressure of O_2. These methods not only provide DCOT, but because acetophenone and light usually excite molecules into their triplet states, because oxygen catalyzes the conversion of singlets into triplets, and because the $S_0 \rightarrow T_1$ absorption populates **6**'s triplet directly they also show that a precursor of DCOT is **6** in its excited triplet state. A detailed study of **6**'s photochemistry will be published separately.

Of the methods available to make DCOT, the one involving irradiation at low temperature (−78 °C) is most convenient for synthesis in quantitity for that involving triplet sensitization is complicated by **2**'s secondary photoreactions, that involving excitation at **6**'s $S_0 \rightarrow T_1$ absorption is inconveniently slow, and that effected under oxygen pressure is difficult to perform. The photolysis at low temperature, when conducted in a variety of solvents, gives **2** as the major product and, as Table I shows, in amounts comparable to the amounts of C_6H_6 isomers (which also form) that increase roughly with the solvent's dielectric constant, with the highest ratio recorded, 60, being in liquid ammonia. (Incidentally, the C_6H_6 isomers including benzene arise directly from **6**, not from **2**, as their amount, compared to **2**, is undiminished when the conversion is low.)

The cleanest solutions of **2** are obtained in acetonitrile, and sometimes such solutions have been used for further work without purification. However, **2** can be purified by either column chromatography (on basic alumina, dichloromethane) or preparative thin-layer chromatography (silica gel PF 254, 1:1 ether–methylene chloride), and it is found to be a highly unstable light yellow oil, soluble in halocarbons and polar solvents (e.g., acetonitrile, DMF), but only sparingly soluble in hydrocarbons.

Its high-resolution mass spectrum establishes its formula as $C_6H_6N_2$ (calcd 106.0531, found 106.0522), and the large fragment ions (100 and 15%) at *m*/*e* 79 and 80 (pyridine and pyridazine) support the structural assignment. The UV ab-

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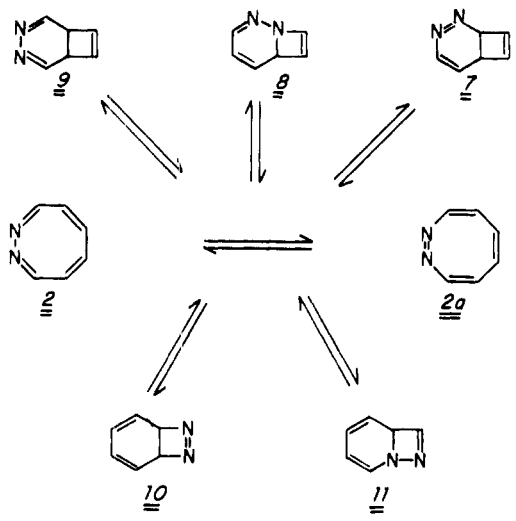
Table I. Ratios of Products of the Photolysis of 6 in Various Solvents[a]

time, h	temp, °C	solvent	dielectric constant[b]	6[h]	e	f		g	DCOT
2	25	THF	7.56	1.3	1	0.5	ND[c]	0.1	3.7
6.5	−40	$CDCl_3$	6.12[d]	8.5	1	0.3	ND	ND	4.8
0.8	25	CD_3CN	37.5[d]	1.5	1	0.9	ND	ND	17
1.5	−40	DMF	52.1	ND	1	ND	ND	ND	24
0.8	−50	NH_3	23	~1	1	ND	ND	ND	~60

[a] Analyses by ^1H NMR spectroscopy are expressed as ratios relative to the moles of benzene. [b] Riddick J. A.; Bunger, W. L. B. "Organic Solvents"; Wiley: New York, 1970. [c] Not detectable. [d] ϵ of nondeuterated compound. [e] Registry no., 71-43-2. [f] Registry no., 5649-95-6. [g] Registry no., 659-85-8. [h] Registry no., 34122-54-8.

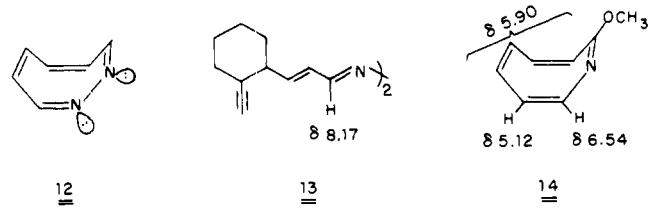
Scheme I



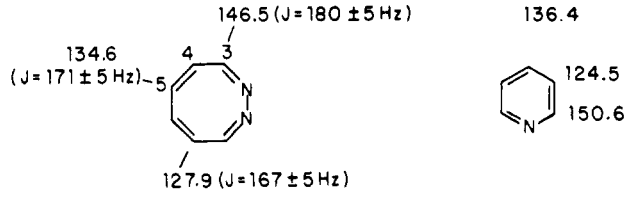
sorption spectrum shows a λ_{max} at 374 nm (log ϵ ~2.3) in addition to end absorption.

Structure of DCOT. While DCOT and the variety of valence tautomers in Scheme I, like cyclooctatetraene and bicyclo[4.2.0]octatriene,[11,12] might quickly equilibrate, the magnetic resonance spectra show that only one species predominates in the mixture and they identify it. Thus, the ^1H NMR spectrum is extraordinarily simple. There is one sharp singlet at δ 6.03 (4 H), which a europium shift reagent[13] splits into an AB quartet (J = 11 Hz), and one broad singlet ($\Delta\nu_{1/2}$ = 4 Hz) at δ 6.93 (2 H), whose width is unaffected by changes in temperature from −75 to +165 °C and unresolved by addition of the shift reagent. This spectrum shows that the bicyclic structures are not present in significant quantity as no saturated C–H resonances are observed, and it distinguishes structures **2** and **2a** because in the tub conformation cyclooctatetraene's adjacent double bonds are almost perpendicular, causing the spin–spin coupling across the single bonds to be small.[12a] The consequence should be to make the resonances of protons not adjacent to nitrogens resemble an AB quartet in **2** and a doublet and a singlet in **2a** and to make the resonance of the protons that are adjacent to the nitrogen in **2** a singlet and in **2a** a doublet. Since the protons next to the nitrogen should be the least shielded, the spectrum shows the dominant structure to be **2**.

If the molecule has this structure and the tub conformation, **12**, the orbitals occupied by the lone pairs of electrons on adjacent nitrogens will be held nearly perpendicular. This might account for what otherwise would be a peculiarity in the chemical shifts: the displacement of the resonance of the proton adjacent to the nitrogen by about 1 ppm to higher fields compared to the analogous resonance in **13**.[14] This shift could be a consequence of the lone pair orbital on one nitrogen delocalizing into the adjacent imine's double bond, which is possible in structure **12**, although not in structure **2a**, and would be analogous to the effect that causes the β-protons in vinylamines,[15] vinylamides,[15] and the 2-methoxyazocine **14**[12a] to resonate at particularly high fields.



The ^{13}C NMR spectrum summarized on structure **15** supports this idea since the resonance of C(3) being approxi-



mately 5 ppm to higher field than in simpler imines (141.7 ± 1.1 ppm)[14] might again reflect the delocalization of the adjacent lone pair electrons, increasing the electron density on that carbon. The basis for the assignment of carbon 3's resonance is the observation that irradiating the proton resonance at δ 6.93 selectively decouples the resonance at 146.5 ppm. Carbon 4 and 5 resonances are assigned by analogy with the spectra of olefins conjugated with electronegative groups like carbonyl or imine and by comparisons, illustrated on structure **16**, with the spectrum of pyridine. The ^{13}C NMR spectrum supports the assignment of structure **2**, and it also shows that the only tautomer present in appreciable quantity is monocyclic.

The enthalpies of formation of the valence tautomers in Scheme I were estimated using group additivity data based on the few experimentally determined relevant heats of formation.[16] These indicate that **2** should be more stable than **2a** by about 8 kcal/mol and that the enthalpy changes accompanying the isomerizations of **2** to the bicyclo[4.2.0]octatrienes should be 0–3 kcal/mol more endothermic than the enthalpy changes accompanying isomerization of the hydrocarbon cyclooctatetraene to bicyclo[4.2.0]octatriene. This accords with the failure to detect by NMR spectroscopy the presence of the valence isomers in samples of DCOT, for the approximately 2×10^{-4}% of bicyclo[4.2.0]octatriene present in COT at 25 °C is similarly undetected.[19] However, these enthalpies of formation fail to account for why refluxing DCOT in dioxane with dimethyl acetylenedicarboxylate, *N*-phenylmaleimide, or *N*-phenyltriazolinedione does not trap any bicyclic tautomers as Diels–Alder adducts as similar experiments with cyclooctatetraene do.[11a–c] Either the valence tautomers are not very reactive toward the dienophiles, or they

Table II. Kinetics of the Thermolysis of 1,2-Diazacyclooctatetraene (2)[a]

temp, °C	first-order rate constants (s^{-1}) × 10^5 for the formation of: benzene	pyridine
140	5.1	6.7
143	9.3	9.9
151	17.2	22.8
165	52.8	57.9
175	190	151

[a] The solvent is *n*-dodecane, and analyses were by vapor phase chromatography.

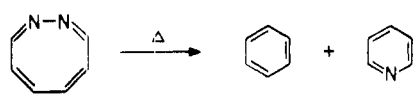
Table III. Activation Parameters for the Decomposition of DCOT[a]

reaction	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
DCOT → benzene	34.4 ± 2	4.8 ± 6
DCOT → pyridine	30.6 ± 2	−4.1 ± 4

[a] Based on the data in Table II.

decompose before they can react, or the valence isomerizations are more difficult than the estimated beats of formation suggest. The last possibility seems unlikely because substituents stabilize the bicyclic tautomers **5** of substituted DCOT's[9] (much as they stabilize the tautomers of substituted cyclooctatetraenes)[12f,20] enough to make the bicyclic structures much more stable than the monocycles. But if the energy changes accompanying isomerization of **2** are much greater than estimated, an interesting reason may be the failure of the estimates to take account of the possibly lesser lone pair–lone pair electron repulsion in **2**, where the lone pairs are held perpendicular, than in tautomers where they are held eclipsed.[21] At present there is no evidence, and it remains for future analysis.

Thermolysis of 2. Heating in *n*-dodecane at 140 °C converts **2** quantitatively, according to NMR and VPC analyses, into benzene and pyridine (eq 2), and not into pyridazine. The



(2)

kinetics in the temperature range from 140 to 175 °C are first order, and Arrhenius plots of the data (Table II), which are linear, provide the activation parameters summarized in Table III. The enthalpies of activation for forming benzene and pyridine differ only slightly, but that the former is somewhat larger is reflected in the ratio of the two products varying with temperature, higher temperature favoring benzene and lower pyridine. No chemiluminescence is observed when the reaction is effected in dodecane containing 9,10-diphenylanthracene or 9,10-dibromoanthracene, although the singlet energies of these molecules are lower than those of the singlet (S_1) and triplet (T_1) of benzene and pyridine.[22]

The way **2** fragments on heating resembles somewhat the way it fragments after being struck by electrons during mass spectrometric analysis (see above), for pyridine cation is a major product and pyridazine cation a small or negligible one in both cases. Benzene, however, is a major contributor to the thermolysis product, although not to the mass spectrum.

Photolysis of 2. Irradiating (λ > 300 nm) DCOT in tetrahydrofuran (THF) gives benzene as the only organic product, and no intermediate is detectable by ^{1}H NMR analysis when the reaction is effected at −50 °C, at which temperature incidentially the transformation is much slower than at room temperature. Also, warming to room temperature after irradiation at −50 °C produces no additional benzene, and hence no intermediate is detectable by this kind of analysis either.

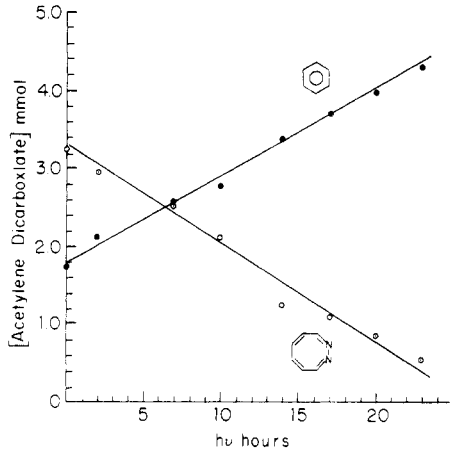


Figure 1. Kinetics of the photolysis of DCOT in THF in the presence of dimethyl acetylenedicarboxylate (DMAD): [DCOT] = 1% w/v; [DMAD] = 10% w/v. The analyses were by ^{1}H NMR, and 1 mmol of dimethylformamide was present as an internal standard.

Table IV. Quantum Yields for Photolysis of 1,2-Diazacyclooctatetraene (2)

sensitizer	triplet energy,[a] kcal/mol	Φ for benzene formation
none		~0.01
xanthone	74	0.5
acetophenone	74	0.8
4-bromobiphenyl	66	0.4
1,4-dibromonaphthalene	60	0.6
β-acetonaphthone	59	0.8
α-acetonaphthone	56	0.7
benzil	53	0.8
fluorenone	53	0.8

[a] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, Calif., 1978; Chapter 8.

Nor is a presumed intermediate, **10**, trapped by dienophiles, like a tenfold excess of dimethyl acetylenedicarboxylate (a dienophile that neither participates avidly in polar reactions nor absorbs the long wavelength irradiating light) or *N*-ethylmaleimide (a more active dienophile that is partially destroyed in side reactions during such experiments), as Figure 1 illustrates. The analyses displayed there show that although much dimethyl acetylenedicarboxylate is present, the sum of the number of moles of DCOT and benzene remains constant during the photolysis, indicating that nothing that forms when the one molecule converts to the other is removed by the dienophile.

DCOT also forms benzene when excited by triplet sensitizers, which as Table IV shows can have triplet energies as low as ~50 kcal/mol and give higher quantum yields than direct photoexcitation. In a benzophenone-sensitized reaction (at −78 °C),[23] just as in the unsensitized photoreaction, no product other than benzene is detected by ^{1}H NMR spectroscopy, nor is additional benzene formed after sensitization when the reaction mixture is rewarmed to room temperature.

In sum, both direct and triplet sensitized irradiations give benzene, and no intermediate, pyridine, or pyridazine is detected.

DCOT neither fluoresces nor phosphoresces at room temperature or at 77 K. The energy of its first excited singlet state

Table V. Peak Potentials in Cyclic Voltammograms of DCOT (2) and Related Compounds

compd	solvent	E_{pa}, V	E_{pc}, V	$E_{pa} - E_{pc}$, V	$E^{\circ\prime}$, V[d]	scan rate, V/s	ref
DMMA[a]	DMF[b]	−1.32	−2.50	1.18	−1.88	4	2b
DCOT	AN[c]	−0.76	−1.78	1.02	−1.27	1	this work
DCOT	DMF	−0.57	−1.66	1.08	−1.12	0.10	this work
DMMA	DMF	−2.0	−2.08	0.08	−2.04	0.24	28

[a] 3,8-Dimethyl-2-methoxyazocine. [b] Dimethylformamide. [c] Acetonitrile. [d] $\frac{1}{2}(E_{pa} + E_{pc})$.

(S_1) was therefore estimated from its absorption spectrum to be ~76 kcal/mol, and that of its first excited triplet state (T_1) was estimated from the energy transfer data in Table IV to be <53 kcal/mol.

Electrochemistry of 2. Polarograms of 1.07 mM DCOT in dry acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte exhibit waves centered on $E_{1/2} = -1.636$ V vs. the standard calomel electrode (SCE) that characterize an irreversible reduction.[24] An estimated diffusion coefficient[26] identifies the number of electrons transferred during the reduction as 2.06, and a plot of log $[i/(i_d - i)]$ vs. E is a straight line, whose slope (αn) measures the electron transfer coefficient α as 0.30.[27]

Cyclic voltammograms measured in acetonitrile using a hanging mercury drop as the working electrode and in dimethylformamide using a planar platinum electrode are summarized in Table V and compared there with the cyclic voltammograms reported for 3,8-dimethyl-2-methoxyazocine (DMMA).[2b,28]

Even in the presence of activated alumina[28] and with the mixed electrolyte $(n\text{-}C_4H_9)_4NClO_4 + (CH_3)_4NBr$, the cyclic voltammograms are not characteristic of quasi-reversible processes, and the waves are elongated as when adventitious protonic materials are present. Although Jensen et al.[28] found the large separations recorded earlier by Paquette et al.[2b] for the cathodic and anodic peaks in the cyclic voltammograms of DMMA to be caused by adventitious protons (from water?), the E° values measured by Jensen and by Paquette are very similar. Accordingly, the values $E^{\circ\prime}$ should not be very different from the potentials for reversible reductions.[29]

Discussion

There seem to be three possible explanations for why pyridine is formed on thermolysis, but not on photolysis, and they are associated with three different rate-determining steps: (1) tautomerization to the bicyclo[4.2.0]octatrienes in Scheme I, (2) fragmentation of the bicyclo[4.2.0]octatrienes, and (3) transformation of **2** to **2a.**

The explanation based on the notion that the tautomerization is the rate-determining step originates from the idea that the transformation to **11** is more facile than that to **10** because the former is a six-electron and the latter a four-electron electrocyclic process.[30] A corrolary is that the photochemical reaction yielding **11** be disfavored, compared to that yielding **10,** because photochemical reactions are facilitated by excited triplet and ground states converging, and this is a feature associated with orbital forbiddenness in thermal reactions.[31] Accordingly, it is reasonable for benzene rather than pyridine to form on photolysis.

If this explanation is correct, the rate-determining step in the thermally induced transformation of DCOT to pyridine should be the formation of **11,** and the enthalpy of activation for the overall reaction (30.0 ± 0.6 kcal/mol, see Table III) would have to be, as it in fact is, similar to that (28.1 kcal/mol)[11a] for the conversion of cyclooctatetraene to bicyclo[4.2.0]octatriene. The enthalpy of activation for forming benzene (34.5 ± 0.5 kcal/mol, Table III) should then also be, as it is, about the same or possibly somewhat greater,[16] the assumption being that the barrier separating **2** and **2a** is lower, which seems likely because the analogous barrier in cyclooctatetraene is 14 kcal/mol[12a,d] and **2** and **2a** probably differ in energy by less than 20 kcal/mol.[16] If they do not, the analysis fails.

The reason pyridazine is not produced might be because acetylene is much more difficult to cleave from the molecules than is nitrogen or hydrogen cyanide, and while this would be true no matter which of the three steps were rate-determining, a failure of all the explanations is their inability to account for why other of the bicyclo[4.2.0]octatrienes (**7, 8,** and **9**) are not observed during the photolyses at low temperature.

The second explanation, based on the hypothesis that fragmentation of the bicyclo[4.2.0]octatrienes rather than their formation is rate-determining, is attractive for its simplicity. It requires only that the activation energy for cleaving N_2 from **10** be less than that for cleaving HCN from **11,** and it accounts for pyridine accompanying benzene during the thermolysis and not during the photolysis by recognizing that the temperature of the latter reaction is lower. This thought is so simple that it is unfortunate the activation data in Table III do not support it, for the difference between the activation enthalpies for forming benzene and pyridine is too small. When the enthalpy (9.9 kcal/mol) and entropy (7 eu) evolved during cyclooctatetraene's transformation into bicyclo[4.2.0]octatriene[11a] are subtracted from the activation parameters in Table III and the small corrections in ref 16 are applied to try to account for the different enthalpies of formation for **10** and **11,**[16] the rate calculated for the formation of benzene from **10** at −75 °C is not, as it would have to be, much greater than that for the formation of pyridine from **11.**

The third explanation, based on the proposition that the rate-determining step in the photochemical transformation is the conversion of **2** to **2a,** is that benzene and not pyridine forms because the conversion of **2a** to **10** is allowed according to the rules of orbital symmetry while that to **11** is not.[30] It has the viture of precedent, for the double bonds do shift when cyclooctatetraenes are exposed to light[12c,f] and they therefore should also in the case of this nitrogen analogue. The reasonableness of **10**'s losing nitrogen was already considered above. The main difficulty with the proposal is that the transformation of **2a** to **10** may be too slow for the formation of **2a** to be rate-determining. Thus, if the enthalpy of activation for the tautomerization of cycloctatetraene (28.1 kcal/mol)[11a] is reduced by 8 kcal/mol (the estimated difference in the enthalpies of **2** and **2a**), the half-life of **2a** at −50 °C would be 10^3 h, which is much longer than the time for appreciable conversion to benzene. But were **2a** much less stable than supposed, compared to **2** and **10,** the transformation to **10** would be faster and the mechanism sustainable.

A reason why **2** might be much more stable than **2a** or **10** is one suggested above to account for the failure to obtain adducts with dienophiles, that lone pairs of electrons on adjacent nitrogens repel each other more if held parallel than if held more nearly perpendicular. This effect should measureably perturb the reduction potential of DCOT if the resulting dianion, like that of other cyclooctatetraenes, is planar.[1] Since the reduction potential of cyclooctatetraene in dimethylformamide has been measured in experiments like those

summarized in Table V to be −1.84 V,[2b] the reduction potential in the absence of a special effect caused by a change in configuration of adjacent nitrogens might be this amount less twice the difference between the similarly determined reduction potentials of 2-methyoxyazocine (−1.62 V) and methoxycyclooctatetraene (−2.06 V).[2b] This is −0.96 V. Alternatively the correction for the two nitrogens might be derived from the potentials measured in dimethylformamide for naphthalene (−1.98 V), isoquinoline (−1.642 V), and phthalazine (−1.432 V).[32] The range of reduction potentials derived in this way, −0.96 to −1.29 V, is large, but it brackets the potential recorded above for DCOT (−1.12 V). Accordingly, while the data are deficient because they could not be measured for reversible reductions, they do not reveal any outstandingly large effect associated with lone pair repulsions.

Thus, the work described above shows the structure of DCOT to be **2** and not **2a** and it shows the bicyclic tautomers, **7–11**, not to be present in appreciable quantity, but it does not reveal the differences in the energies or the barriers to the interconversions.

Experimental Section

Electronic absorption spectra were recorded on Cary-17 instruments, emission spectra on a Perkin-Elmer Model MPF-3L spectrofluorimeter, and ^{1}H NMR spectra on Varian A-60, HA-100, or XL-100 spectrometers or a Jeolco MH-100. Vapor phase chromatography (VPC) analyses were performed on a Hewlett-Packard Model 5750 vapor chromatograph with a flame ionization detector. The chromatographic column was 3 ft × 0.25 in. 5% isodecyl phthalate–1.25% triethanolamine on Chromosorb W. The benzene isomers were analyzed on this column at 22 °C and benzene, pyridine, and azo compounds **2** and **6** at 110 °C. Photoirradiations were conducted using a 450-W medium-pressure mercury lamp or 450- or 1000-W high-pressure xenon mercury lamps and appropriate Corning glass filters. Direct irradiation into the $S_0 \rightarrow T_1$ band was effected using a Coherent Radiation Model 52 argon laser tuned to 490 nm. Irradiations under 1400 psi of oxygen were conducted in a special steel cell with a quartz window.

Solvents were distilled once before they were used. Ether–pentane–ethanol (MCB phosphorimetry grade) and 3-methylpentane (Aldrich 99+%) used for low-temperature study were passed once through an alumina column.

Synthesis of Diazacyclooctatetraene 2. (a) Irradiation of 6 at −78 °C. A solution of 1 g (0.95 mmol) of azo compound **6** in 100 mL of methylene chloride, cooled to −78 °C by a dry ice–acetone bath, was irradiated using a 450-W medium-pressure mercury lamp for approximately 6 h. The solvent was then evaporated under reduced pressure, and the resulting viscous yellow oil, after purification by column chromatography (silica gel–methylene chloride), gave about 0.8 g of **2** (80% yield) as a light yellow oil. It could also be isolated by preparative thin-layer chromatography (TLC) (silica gel PF 254, 1:1 ether–methylene chloride).

(b) Sensitized Irradiation of 6 at 22 °C. About 50 mg of **6** in 10 mL of methylene chloride was irradiated in the presence of 10 mg of acetophenone for about 3 h. Purification by column chromatography gave about 20 mg of **2**.

(c) Direct Irradiation into the $S_0 \rightarrow T_1$ Band. About 5 mg of **6** in 10 mL of methylene chloride was irradiated for 10 h at 490 nm in a cell with a path length of 10 cm. Analysis by VPC showed **2** to be the major product.

(d) Irradiation of 6 under Oxygen Pressure. About 10 mg of **6** in 10 mL of methylene chloride was irradiated for about 4 h under 1400 psi of O_2 in a steel cell equipped with quartz windows. Analysis by VPC showed **2** to be the major product.

(e) Irradiations in Various Solvents. An NMR tube containing a solution of ~100 mg of azo compound **6** in trideuterioacetonitrile under nitrogen was placed in a Dewar flask containing methanol at −50 to −40 °C and irradiated through a Pyrex filter for 50 min. A ^{1}H NMR spectrum was then measured at ambient temperature. The results of this and similar experiments employing other solvents are listed in Table I.

(f) Irradiation in Liquid Ammonia. Approximately 11 mg of azo compound **6** in freon was placed in an NMR tube, and the solvent was evaporated under a stream of nitrogen. Ammonia was distilled from potassium into this septum-capped NMR tube at −78 °C and the resultant solution irradiated at −50 to −40 °C through Pyrex for 50 min. An NMR spectrum was then measured at −50 °C, and the results are also summarized in Table I.

Thermolysis of 2. A solution of **2** in dodecane was degassed, sealed in vacuo in an NMR tube, and heated in a thermostated oil bath. The kinetics of the appearance of benzene and pyridine were measured by VPC analyses (dioxane internal standard) after the tube was periodically quenched in an ice bath. NMR analyses of the 140 °C run revealed similar kinetics.

Photolysis of 2. Quantum yields for the conversion of **2** to benzene were measured by irradiating degassed 0.01 M hexane solutions containing various sensitizers (Table IV). Irradiations were conducted in a "merry-go-round" apparatus,[33] and the conversion of valerophenone to acetophenone[34] was used as the actinometer (Φ = 0.33 in benzene). All samples were analyzed by VPC when the conversion was ≤5%; dioxane was the internal standard.

Photochemical Trapping Experiment. A sample of 75.7 mg of **6** was dissolved in 1.6 mL of dry tetrahydrofuran (THF) and photolyzed at −50 °C, and the resulting solution of DCOT (56% DCOT, 19% azo compound **6**, 15% benzene, 8% Dewar benzene, and 2% benzvalene) was added to a solution of 995 mg (7 mmol) of distilled dimethyl acetylenedicarboxylate (DMAD) in 5 mL of dry THF. Enough THF was then added to make the total volume 8.6 mL (1% DCOT, 10% DMAD). Then 77.4 μL (73 mg, 1 mmol) of dimethylformamide (DMF) was added as an internal standard, and the solution was irradiated through a Pyrex filter at −50 °C for a total of 23 h while the appearance of benzene and the disappearance of DCOT were periodically monitored by NMR analysis. No evidence for an adduct was detected in the NMR spectrum nor by TLC.

Preparation of DCOT in Acetonitrile for Electrochemistry. A solution of 10.5 mg (0.1 mmol) of **6** in 600 μL of deuterioacetonitrile was irradiated through Pyrex (medium-pressure Hanovia lamp) at −50 °C for 50 min. The NMR spectrum of the solution showed that **6** was no longer present and that the conversion to DCOT was ~85% (integration relative to the solvent's residual protons).

Electrochemistry in Acetonitrile. Electrochemical experiments were performed using a PAR 170 electrochemistry system and a standard H-type polargraphic cell filled on both sides with acetonitrile[35] solutions 0.1 M in tetrabutylammonium perchlorate. In one side was placed a commercial aqueous saturated calomel electrode (SCE), and in the other side was placed a platinum auxilliary electrode, dropping mercury electrode, and nitrogen deaeration system. A background polarogram was recorded, and then after 100 μL of the deuterioacetonitrile solution of DCOT was added, thereby making the cell 0.54 mM in DCOT, a polarogram was measured: $E_{1/2}$ = −1.64 V, $i_d \cong$ 10.6 μA. Another 100 μL of the solution of DCOT in deuterioacetonitrile was then added, making the cell 1.07 mM in DCOT. A polarogram was again measured, yielding the following data: m = 3.3 = mg/s, t = 1.7 s/drop, i_d = 18.6 μA, $t_{1/2}$ = 1.9 s/drop, $E_{1/2}$ = −1.636 V, $E_{1/4}$ = −1.590 V, $E_{3/4}$ = −1.685 V. A polarogram was recorded on an expanded scale so that $E_{1/2}$ and αn could be determined from a log plot. The dropping mercury electrode was then replaced by a hanging mercury drop electrode, and a cyclic voltammogram was recorded, yielding the following data: E_{pc} = 1.785 V, E_{pa} = −76 V, scan rate 1.0 V/s. The cyclic voltammogram was very sensitive to oxygen impurities, and the cell had to be deaerated with nitrogen for 5 min before each run.

Electrochemistry in Dimethylformamide (DMF). The electrochemical experiments were performed using a PAR 173 potentiostat with a PAR 175 universal programmer in a standard four-point electrochemical cell fitted with a platinum wire counter electrode, a nitrogen deaeration inlet, a cracked glass junction to the SCE, and a 1.4-mm d. platinum disk working electrode. The spectrograde DMF was dried over activated alumina after predrying with 4 Å molecular sieves. All electrolytes were dried overnight at 60–70 °C at 0.1 torr. After the solution to be electrolyzed was added to the cell, so was activated alumina. A background scan run on a DMF solution 0.1 M in tetrabutylammonium perchlorate and saturated in tetramethylammonium bromide, but before DCOT was added, revealed a constant background of 1.5 μA. A 52-μL portion of a DMF solution prepared by photolyzing 35.4 mg of azo compound **6** in 700 μL of DMF at −50 °C as previously described was added to the cell, making it 0.91 mM in DCOT. A cyclic voltammogram was run at a scan rate of 100 mV/s and repeated after the DCOT concentration was doubled and tripled. No iR compensation was necessary. The data are presented in Table VI.

A calculation[36] of the current expected for a 0.9 mM solution assuming α to be 0.5 and the number of electrons to be 2 is 13 μA.

A second experiment was performed under the same conditions but with even greater care to exclude water. A 3.8-mm d. platinum disk

Table VI

[DCOT], mM	E_{pc}, V	E_{pa}, V	$^{i}E_{pc}$, μA
0.91	−1.60	−0.58	11
1.82	−1.63	−0.58	23
2.73	−1.66	−0.57	34

Table VII

[DCOT], mM	E_{pc}, V	E_{pa}, V	scan rate, mV/s
0.91	−1.67	−0.60	100
1.82	−1.70	−0.61	100
1.82	−1.74	−0.57	500
1.82	−1.88	−0.40	2000

working electrode was substituted for the smaller one used before. Again, no iR compensation was necessary. The results are in Table VII.

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Registry No.—**2**, 292-69-3; pyridine, 110-86-1.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of DCOT (**2**) (1 page). Ordering information is given on any current masthead page.

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