

MNDO Calculations for the Dehydrocyclooctatetraenes<sup>1</sup>

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**Abstract:** MNDO, UMNDO, and MNDO/CI calculations are reported for the four didehydrocyclooctatetraenes and the bicyclic valence tautomers, pentalene, benzocyclobutadiene, and bicyclo[5.1.0]octatetraene. MNDO predicts that bicyclo[5.1.0]octatetraene should be as stable as the parent didehydrocyclooctatetraene, cyclooctatrienyne, which is known to exist. Two novel cyclic diallenes formed by conrotatory or disrotatory ring opening of benzocyclobutene are also predicted by MNDO to be stable species.

While evidence has been presented<sup>2</sup> for the existence of 1,2-didehydrocyclooctatetraene (**1**) as a reaction intermediate and while several derivatives of **1** have been characterized,<sup>3</sup> none of the other three monocyclic didehydrocyclooctatetraenes (DDCOT; **2-4**) have as yet been reported. However, the latter can also exist as bicyclic valence tautomers, bicyclo[5.1.0]octatetraene, (**5**), benzocyclobutadiene (**6**), and pentalene (**7**). While **5** is also unknown, **6** and **7** have been the subject of much interest in recent years in view of their expected antiaromaticity. Thus **6** contains a cyclobutadiene ring while **7** is in effect planar cyclooctatetraene, the transannular bond playing only a steric role.<sup>4,5</sup> While **6** has been prepared,<sup>6</sup> it dimerized too rapidly for its properties to be determined, while **7** has been obtained only as the dianion.<sup>7</sup> Stable derivatives of **7** have, however, been described,<sup>8</sup> dimerization being inhibited by introduction of bulky substituents.

While calculations have been reported for the didehydrobenzenes<sup>9</sup> (benzynes) and also for the bicyclooctatetraenes **6**,<sup>10</sup> **7**,<sup>11</sup> and **5**<sup>12a,b</sup> theoretical studies of the monocyclic DDCOTs have so far been limited to **1**.<sup>12c</sup> No calculations on the monocyclic isomers **2-4** have appeared in the literature. The calculations for **6** and **7** have moreover been concerned primarily with their antiaromaticity. As yet no attention seems to have been paid to the DDCOT system as a whole, in particular to the relative stabilities and interconversion of the monocyclic and bicyclic valence tautomers. Here we report a detailed study of **1-7** and several related compounds, and of their relevant interconversions, using MNDO.<sup>13</sup>

Chart I

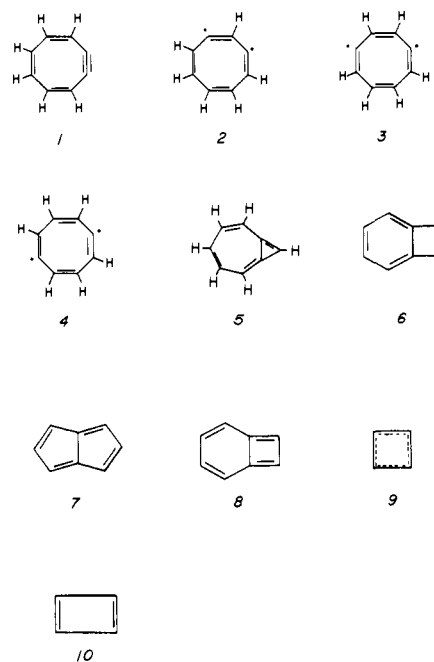


Table I. MNDO Heats of Formations for 1-8, 11, and 12 (kcal/mol) with UMNDO Triplet Energies in Parentheses

compd	RHF	UHF	HE/CI
<b>1</b>	121.45	104.51 (126.56)	125.55
<b>2</b>	<i>b</i>	125.42 (141.74)	<i>c</i>
<b>3</b>	<i>b</i>	108.75 (120.37)	143.71
<b>4</b>	<i>b</i>	117.71 (133.03)	141.12
<b>5</b>	124.92	109.86 (126.01)	130.32
<b>6</b>	90.97	79.15 (100.7)	94.31
<b>7</b>	87.34	70.67 (88.26)	90.74
<b>8</b>	117.34	<i>a</i>	118.13
TS 7-4		125.76	
TS 6-3	147.56	123.28	
TS 5-2		135.57	
<b>11</b>	135.3	<i>a</i>	134.08
<b>12</b>	127.99	<i>a</i>	128.1
<b>16</b>	130.95	130.95	134.80

<sup>a</sup> Does not exist on the UMNDO surface. <sup>b</sup> Does not exist on the MNDO surface. <sup>c</sup> Does not exist on the MNDO/HE/CI surface.

## Procedure

The calculations were carried out by using the standard MNDO method<sup>13</sup> as implemented by the MOPAC<sup>14</sup> program. Since the C<sub>8</sub>H<sub>6</sub> potential energy (PE) surface involves biradical-like species, the calculations were repeated by using the spin-unrestricted<sup>15</sup> version (UMNDO)

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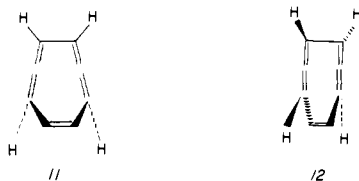
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of MNDO. UMNDO is known to give heats of formation for biradicals that are too negative by ca. 1 eV, due to overestimation of the correlation energy.<sup>16</sup> Better results are obtained by using the "half-electron"<sup>17</sup> version of MNDO, particularly if  $3 \times 3$  CI is included<sup>18</sup> (MNDO-HE-CI). This improvement is, however, achieved only at the expense of a massive increase in computing time, due to the extra time needed to calculate derivatives of the energy.<sup>19</sup> The problem was minimized in the present case by using the UMNDO geometries as the starting geometries in the MNDO-HE-CI calculations. Reactions were followed by the reaction coordinate method,<sup>20</sup> with an appropriate internuclear distance as the reaction coordinate. Transition states (TS) found in this way were refined and characterized by the McIver-Komornicki<sup>21</sup> procedure.

## Results

Calculations were first carried out for **1-7**, using MNDO, UMNDO, and MNDO/HE/CI. All three procedures predicted **1** and the bicyclic species **5-7** to be minima on the  $C_8H_6$  potential energy (PE) surface. Their calculated heats of formation are shown in Table I. Since the difference between the MNDO and UMNDO values is  $<20$  kcal/mol, it can be concluded that all four compounds are normal closed-shell species, a conclusion supported by the fact that the MNDO-HE-CI energies are more positive than the MNDO ones. This is commonly the case for closed-shell species, because while HE MOs are good for describing biradicals or excited states they are less appropriate for ground states. The heats of formation of the triplet excited states for **1-7** were calculated and the results are also given in Table I. Calculations were also carried out for the quinonoid valence tautomer (**8**) of **6** and for the bisallenic structures **11** and **12**. All three corresponded to a minima on the MNDO and MNDO-HE-CI PE surfaces but not on the UMNDO one.



## Discussion

The most interesting conclusions from these calculations are that **5**, **11**, **12**, and **16** should be stable species. First, however, we will discuss benzocyclobutene (**6**) and pentalene (**7**) since they, or their derivatives, are known compounds whose chemistry has been studied.

**Benzocyclobutadiene (6).** Figure 1 shows the bond lengths calculated for **6** and **8** by MNDO and MNDO-HE-CI. Both procedures agree in predicting the bond lengths in both isomers to alternate strongly, the values differing little from those observed for single (1.46–1.48 Å) and double (1.35 Å) bonds in classical polyenes. While such an alternation would be expected in **8** if it is indeed a stable species, the six-membered ring being quinonoid, it is surprising to find a similar alternation predicted for the benzenoid ring in **6**. Its chemical behavior is, however, consistent with this formulation. The fact<sup>6</sup> that **6** acts as an extremely powerful dienophile in the Diels-Alder reactions would be difficult to explain if the benzene ring in it were already fully aromatic.

The alternation of bonds in **6** can be explained convincingly in terms of PMO theory.<sup>4,5</sup> The aromaticity/antiaromaticity of symmetrical cyclic polymethines is predicted to decrease with ring size, so the antiaromatic energy of square cyclobutadiene (**9**) should be greater than the aromatic energy of benzene. Since the difference in energy between **9** and the rectangular ground state (**10**) seems to be only about 10 kcal/mol,<sup>22</sup> even **10** should

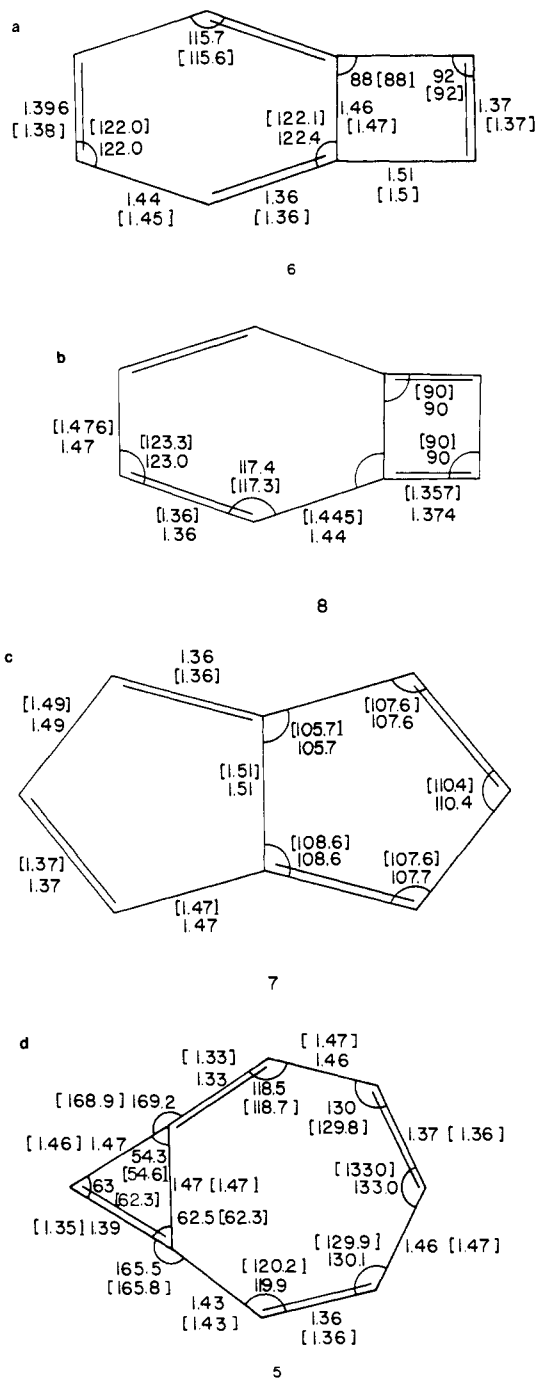


Figure 1. MNDO/HE/CI and [MNDO/RHF] geometries for **5-8**.

have a large antiaromatic energy, a conclusion supported by the following estimate.

The heat of formation of **10** is calculated<sup>22,23</sup> by MINDO/3 to be 92 kcal/mol. Since MINDO/3 performs better than MNDO for compounds containing four-membered rings,<sup>24</sup> the MINDO/3 value is probably near to the truth. The heat of formation of "classical" cyclobutadiene, minus its strain energy, should differ from that of *cis*-1,3-butadiene (29 kcal/mol) by the same amount (4 kcal/mol<sup>25</sup>) that the latter differs from two molecules of ethylene. The strain energy can be estimated to be

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24 kcal/mol by using the CCC bending force constant from a recent analysis<sup>26</sup> of the heats of formation of small-ring compounds, where  $\sigma$  aromaticity was taken into account. The heat of formation of classical **10** should therefore be  $29 + 4 + 24 = 57$  kcal/mol. The antiaromatic energy of **10** is then  $92 - 57 = 35$  kcal/mol, which is much greater than the aromatic energy (21 kcal/mol<sup>27</sup>) of benzene.

The transannular bond in **6** is therefore expected to have minimal  $\pi$ -bond character, as indeed is indicated by its calculated length (1.46 Å; Figure 1a) which corresponds to that of a single C-C bond in a classical polyene. Since **8** contains an intact **10** ring, it should be correspondingly less stable than **6**. The difference (26 kcal/mol) between the heats of formation calculated (Table I) for **6** and **8** is indeed comparable with the estimated antiaromatic energy of **10**.

**Pentalene (7)**. Figure 1c shows the geometry calculated for **7** by MNDO. In agreement with previous calculations,<sup>11</sup> the bonds in it are predicted to alternate, as would be expected since it represents a mildly perturbed form of (antiaromatic) planar cyclooctatetraene.<sup>4,5</sup> The transannular bond is predicted to be longer (1.51 Å) than a normal "polyene" single bond (1.46 Å). The difference can be attributed to ring strain, the bond angles in **7** being much less than the value ( $120^\circ$ ) normal for  $sp^2$  carbon.

The strain energies of **6** and **7**, estimated as above, are 24 and 10 kcal/mol, respectively. If **6** were likewise a mildly perturbed cyclooctatetraene, it should then be higher in energy than **7** by 14 kcal/mol. While MNDO predicts **7** to be the most stable DDCOT isomer, the difference between the heats of formation calculated for **6** and **7** is only 3.6 kcal/mol. The difference (10 kcal/mol) can be attributed, at least partly, to the aromaticity of the vestigial benzene ring in **6**.

**Bicyclo[5.1.0]octatetraene (5)**. The third bicyclic isomer, **5**, is predicted to be higher in energy than **7** by 37.6 kcal/mol, due to its much greater strain energy. The magnitude of this is difficult to assess because it will be partially offset by the  $\sigma$  aromatic<sup>26,28</sup> energy of the three-membered ring. However, the net effect of ring strain and  $\sigma$  aromaticity in **5** is likely to be similar to that in cyclopropene, the conventional strain energy<sup>26</sup> of which is 54 kcal/mol. Figure 1d shows the geometry calculated for **5**.

The relationship between **5** and **1** is similar to that between *m*-benzyne and *o*-benzyne, the former being likewise predicted, by MNDO,<sup>29</sup> to be bicyclic and unexpectedly stable.<sup>29</sup> Since *m*-benzyne has been shown to exist as a reaction intermediate,<sup>30</sup> and since **1** is known,<sup>2</sup> it seems likely that **5** will also prove to be a relatively stable reaction intermediate.

**Cyclooctatrienyne (1)**. As indicated above, the monocyclic DDCOT (**1**) is also predicted to have a closed-shell structure. Its MNDO geometry, shown in Figure 2a, corresponds, as expected, to cyclooctatrienyne, the ring containing three double bonds and one triple bond. Such a system would be expected to be highly strained. The tendency of the triple bond to be linear indeed forces the molecule into adopting a planar structure, in spite of the resulting antiaromaticity due to cyclic conjugation. MNDO predicts it to be a very unstable species, its calculated heat of formation (Table I) being almost as great as that of **5**. In spite of the instability of **1** relative to the rest of the  $C_8H_6$  PE surface **1** has been experimentally generated and then trapped.<sup>2</sup>

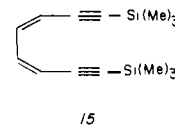
**Other Didehydrocyclooctatetraenes**. The other three monocyclic DDCOTs, **2-4**, are predicted, by UMNDO, to be biradicals, using this term loosely to describe species best formulated as such. None of them corresponds to a minimum on the MNDO potential surface. Their UMNDO heats of formation (Table I) are, however, surprisingly low, implying a significant stabilizing interaction between the radical centers. For example, the difference between the MNDO energy for **7** and the UMNDO one for **4** is only 30

kcal/mol. Even allowing 25 kcal/mol for the underestimation of molecular energies by UMNDO and 10 kcal/mol for the strain energy in **7**, the corrected difference still amounts only to 45 kcal/mol, which is much less than the bond energy of an  $sp^2-sp^2$  C-C bond (ca. 90 kcal/mol).

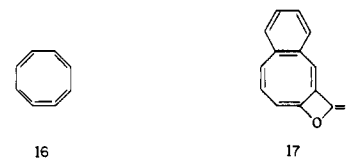
Some years ago MINDO/3<sup>31a</sup> and INDO<sup>31b</sup> calculations led to the surprising conclusion (confirmed by later work<sup>32</sup>) that cycloheptatrienacarbene (**13**) in fact exists as a cyclic allene, cycloheptatetraene (**14**). We have now likewise found that the biradical (**3**) in fact exists as one or other of two isomeric cyclic bisallenes, one (**11**) with  $C_7$  symmetry and the other (**12**) with  $C_2$  symmetry, interconvertible only by rotation about C=C double bonds. Their calculated geometries are shown in parts b and c of Figure 2 and their heats of formation in Table I. To our surprise **12** was the more stable, by 7.3 kcal/mol. Further examination showed that the difference is due to transannular interactions between  $C_5H$  and  $C_8H$  in **11**, which lead to twisting, and consequent weakening, of the 5-6 and 7-8 carbon-carbon bonds. This conclusion was confirmed by energy partitioning within the MNDO formalism, which indicated that these bonds are stronger in **12** than in **11**.



Mitchell and Sondheimer<sup>33</sup> obtained 0.5% of cyclooctane as a byproduct in the catalytic reduction of 1,8-bis(trimethylsilyl)octa-3,5-dien-1,7-diyne (**15**) and suggested that it might have been formed via **11** or **12** as an intermediate. It seems more likely that the reaction involved a concerted reduction-cyclization.



Another  $C_8H_6$  molecule is 1,2,3,5,7-cyclooctapentaene (**16**), which is the cumulene valence isomer of **1**. In order to obtain a reasonable geometry of **16** an MM2<sup>34</sup> calculation was first carried out via the MODEL<sup>35</sup> program. The optimized MM2 geometry was then used as the starting point for the MNDO calculation. While Huang et al.<sup>12c</sup> had failed to find a minimum corresponding to **16**, its MNDO heat of formation was only 9.5 kcal/mol greater than that of **1**. The geometry for **16** is given in Figure 2d and the heat of formation for **16** is given in Table I. Using the optimized MNDO geometry for **16** as the starting point for a MINDO/3 calculation, we were also able to locate **16** as a minimum on the MINDO/3 PE surface. Using the MINDO/3 results of Huang et al.<sup>12c</sup> for the heat of formation of **1** (107.6 kcal/mol), we find that MINDO/3 also predicts **16** to only be slightly less stable (by 8.4 kcal/mol) than **1**.



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(b) Tyner, R. L.; Jones, W. M.; Öhrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765.

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(34) See, e.g.: Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D.C., 1982; A.C.S. Monograph 177.

(35) The MODEL program is a graphical input/MM2 optimization program developed by Clark Stillé. The version used here was modified for use on our Tektronix terminals and our VAX 11/780 computer. Also, the modified version of MODEL will now dump out a data file suitable for running in our MOPAC program.

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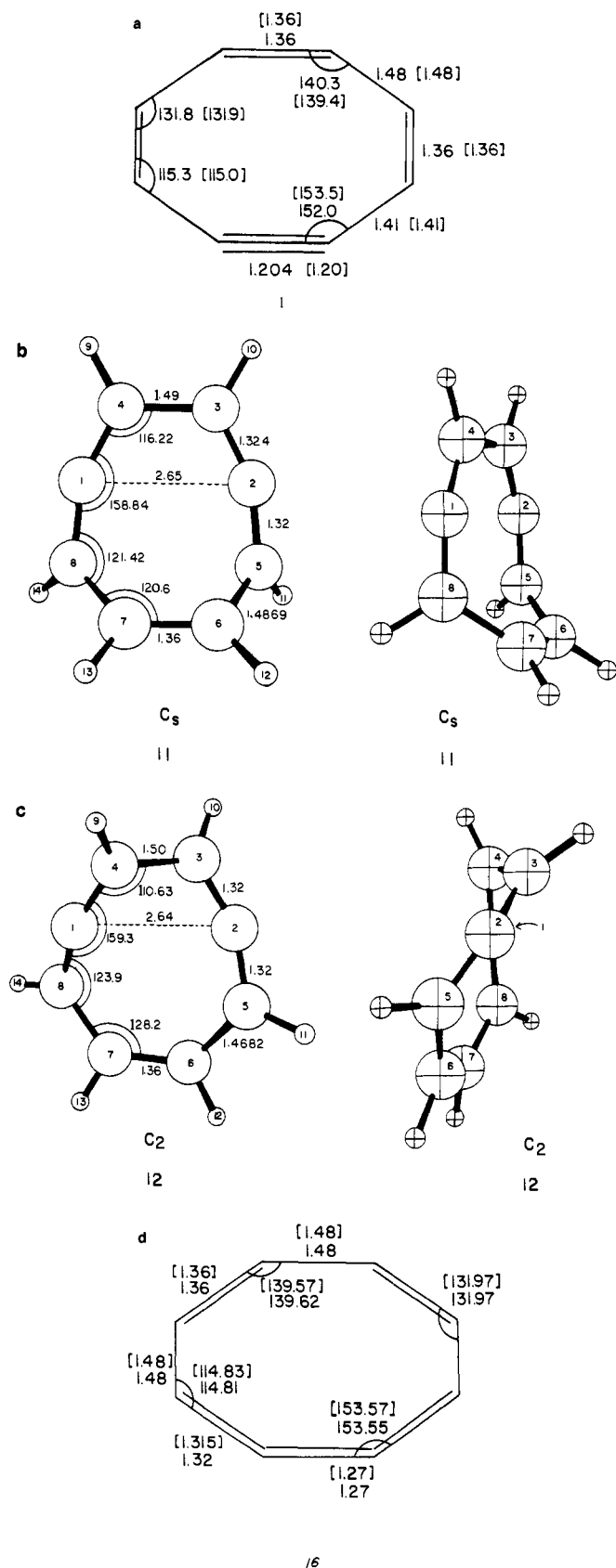


Figure 2. MNDO/RHF geometries for 1, 11, 12, and 16.

The valence isomerization of **16** to **1** is also of interest. The orbital correlation diagram (OCD) for this process is given in Figure 3, where since both **1** and **16** have  $C_{2v}$  symmetry we chose the plane bisecting either the triple bond (in **1**) or the central cumulated double bond (in **16**, see Figure 3). It is readily apparent, from the OCD, that the valence isomerization of **16** to

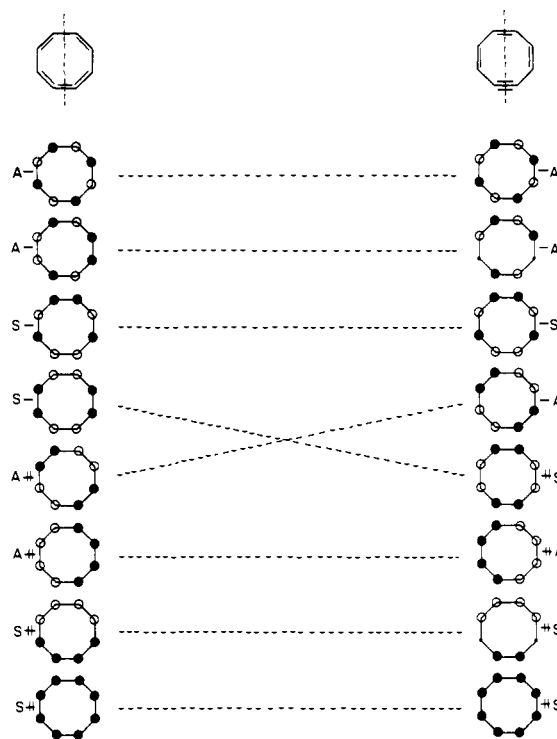


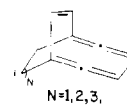
Figure 3.

**1** is a "forbidden" process. Hence, once **16** is generated its isomerization to **1** should be slow. In order to test this conclusion we attempted to locate the TS for the valence isomerization of **16** to **1**. Reaction path calculations immediately showed that an orbital crossing is involved in this situation, the HOMO of **16** evolving into the LUMO of **1** along the reaction path.

The possible stability of **16** could be most easily studied by using benzannulation to force its formation. Photolysis of **17** should, for example, give a benzene derivative of **16**.

**Reaction Paths.** The conversions of **2** to **5** and of **4** to **7** were next studied by using UMNDO and taking the length of the transannular bond in **5** or **7** as the reaction coordinate. Table I shows the heats of formation calculated for the corresponding transition states. The barrier to conversion of **2** to **5** is predicted to be only 10 kcal/mol. Since **5** is a closed-shell species, the TS for its formation from **2** will have much less biradical character than **2** and the barrier to conversion of **2** to **5** should be correspondingly less than 10 kcal/mol, because of UMNDO's known propensity to overstabilize biradicals.<sup>16</sup> Consequently, **2** may not even be a stable species. Indeed, the fact that it is not a minimum on the MNDO-HE-CI PE surface suggests that this is the case. Similar remarks apply even more forcefully to **4**, the UMNDO barrier to cyclization (8 kcal/mol) being still smaller. Hence, it seems unlikely that **4** corresponds to a true minimum.

Conrotatory ring opening in benzocyclobutene (**6**), forming **12**, should be "allowed", while disrotatory conversion to **11** should be "forbidden". Ring opening in **6** is indeed predicted to give **12**, the activation energy for the reverse process being 19.57 kcal/mol. From analogy with cyclobutene,<sup>36</sup> the activation energy for conversion of **11** to **6** is likely to be greater by ca. 14 kcal/mol than that for **12** so **11** may be a relatively stable species, especially if ring closure is inhibited by suitable steric restraints. A possible objective for synthesis might, for example, be **18**.



18

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**Triplets.** As noted above all of the molecules studied here are ground-state singlets, the triplets being excited states. Energies are given in Table I, and since the geometries presented no unusual features they are not given in the text.

**Cartesian Coordinates.** For all of the molecules studied in this manuscript we are including as supplementary material their cartesian coordinates.

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**Supplementary Material Available:** Listing of Cartesian coordinates for compounds 1-8, 11, and 12 (17 pages). Ordering information is given on any current masthead page.

## Evidence for Triplet State Sublevel Selective Photochemistry in Phthalazine

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**Abstract:** The relative sublevel populating rates for the photoexcited triplet-state zero-field sublevels of phthalazine in 2-octanol have been found to be unequal, as determined via ODMR. Hence, the explanation proposed by Basu et al.<sup>2</sup> to rationalize the lack of TM spin polarization in the reaction between photoexcited phthalazine and 2,6-di-*tert*-butylphenol in 2-octanol appears unfounded. We propose a kinetic model where sublevel selective rates for hydrogen abstraction lead to an attenuation of TM polarization. The mechanism for sublevel selectivity is based upon the enhanced reactivity of  $n,\pi^*$  states toward hydrogen abstraction, *vis-à-vis*  $\pi,\pi^*$  states, and the unequal admixture of  $n,\pi^*$  character into each zero-field sublevel of the predominantly  $\pi,\pi^*$  phthalazine  $T_1$  state. Calculations indicate a fivefold decrease in TM polarization for phthalazine (compared to the case of no sublevel selectivity), but only a twofold decrease for quinoxaline, where a TM polarization pattern has been observed.

The photoexcited triplet state of any organic molecule is composed of three nearly degenerate but quite distinct magnetic sublevels. These sublevels arise from the fact that, in the absence of an external magnetic field, the total spin angular momentum of the triplet state may be quantized in one of three mutually perpendicular planes, generally associated with symmetry elements of the molecular framework.<sup>3</sup> The energy splittings of the three sublevels are largely caused by the dipolar interactions of the unpaired electrons' magnetic moments and arise from differences in average interelectron distances in the three zero-field spin states.

A striking variation in behavior between the sublevels concerns the rates of intersystem crossing (isc) to and from each sublevel. Relative rates often vary by factors up to 100 for this spin-forbidden process. These differences can be ascribed to the varying admixtures of singlet character, via spin-orbit coupling, into the sublevels due to their different symmetry properties.<sup>4</sup>

The unequal isc rates of the sublevels may be exploited to determine their individual photophysical parameters via optically detected magnetic resonance spectroscopy (ODMR).<sup>5,6</sup> Here, the populations of the zero-field sublevels of a phosphorescent triplet state are probed by inducing transitions between sublevels via application of resonant microwave radiation (zero-field splittings are typically 0.1 to 10 GHz). The population transfer is observed by detecting changes in the phosphorescent intensity

of the sample, which arise from the differential propensity of each sublevel to radiate to the ground state.

A second consequence of differential intersystem crossing is the phenomenon of triplet mechanism (TM) polarization of the ESR spectra of the free radical products obtained from the reaction of photoexcited triplet states, referred to as TM chemically induced dynamic electron polarization (CIDEP).<sup>7</sup> Sublevel selective isc from the photoexcited  $S_1$  state creates an initial non-Boltzmann population distribution in the  $T_1$  sublevels. This zero-field distribution is "carried over" to the high-field triplet states, which exist in the external ESR magnetic field. The triplet spin polarization may be converted to a doublet spin polarization via chemical reaction of the triplet, often by hydrogen abstraction. Thus, one may observe electron spin resonance signals with either enhanced absorption or emission, relative to the intensity expected for the thermal distribution of radical spin states.

The photochemistry<sup>8</sup> and photophysics<sup>9</sup> of "mixed" excited states have been the subject of much recent investigation. In such molecules, typically with carbonyl or azine chromophores, the lowest excited state is not purely  $n,\pi^*$  in nature but exhibits properties consistent with varying admixtures of both states. The consequences of excited-state mixing in triplets have become manifest in such phenomena as the rate of hydrogen abstraction,<sup>10</sup> variations in the zero-field splitting parameters,<sup>11</sup> and ESR TM polarization.<sup>12</sup>

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