

sented in this study provide the first direct evidence for the intermediacy of the nitroaromatic anion in the photoreduction of aromatic nitro compounds in 50% IPA-water containing HCl.

A. Cu, A. C. Testa*

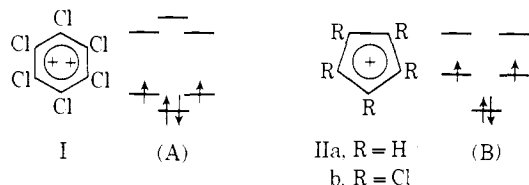
Department of Chemistry, St. John's University
Jamaica, New York 11439

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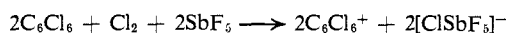
Dipositive Ion of Hexachlorobenzene. A Ground-State Triplet

Sir:

We have prepared the dipositive ion of hexachlorobenzene (I) by a two-step oxidation of the parent HCB. This ion is the first example of a benzene system having four π -electrons (A).¹ As predicted by simple Hückel theory, I is a ground-state triplet. The two unpaired electrons occupy degenerate orbitals and the molecule retains the sixfold symmetry of the parent. In contrast to I a Jahn-Teller distortion to lower symmetry can occur in the monopositive² and mononegative³ ions as well as the excited states⁴ of benzene. The π -electron configuration of I parallels that of the cyclopentadienyl cations⁵ (II) which also have triplet ground states (B).



Solid HCB was mixed at room temperature with a viscous solution of SbF_5 saturated with Cl_2 .⁶ A deep purple coloration appeared and the resulting solution gave a strong esr signal at $g = 2.0156$. The most likely origin of this resonance is $\text{C}_6\text{Cl}_6^{2+}$. Assuming the stoichiometry



the signal intensity indicates that, within a factor of ~ 1.5 , 40% of the C_6Cl_6 has reacted by this path. Upon cooling to 5 or 77°K and irradiation with light of $\lambda > 3100 \text{ \AA}$, an esr signal (Figure 1) characteristic of a

(1) A stable dication, $(\text{C}_5\text{H}_5)^{2+}$, has been observed by H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973). This singlet species consists of a CH_2C^+ fragment interacting with a pentamethylcyclopentadienyl cation to form a pentagonal pyramid. The nmr observations preclude the possibility of a triplet electronic system so that this pyramidal structure is distinct from I.

(2) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 292 (1967). Apparent sixfold symmetry is seen in the monocation and anion³ presumably due to averaging over the distorted configurations.

(3) M. R. Das, S. B. Wagner, and J. H. Freed, *J. Chem. Phys.*, **52**, 5404 (1970), and references cited therein. R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Amer. Chem. Soc.*, **86**, 520 (1964).

(4) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, 1966, pp 473-495.

(5) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **89**, 1112 (1967); M. Saunders, R. Berger, A. Jaffee, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *ibid.*, **95**, 3017 (1973).

(6) The combination of Cl_2 and SbF_5 appears to be an unusually strong oxidizing agent. We observed no coloration upon the addition of BF_3 or AlCl_3 to suspensions of C_6Cl_6 in liquid Cl_2 (-40°). However, the addition of SbCl_5 to C_6Cl_6 and SbF_5 was able to generate the same purple color and I. The reaction of these two antimony pentahalides is exothermic and may be complex.

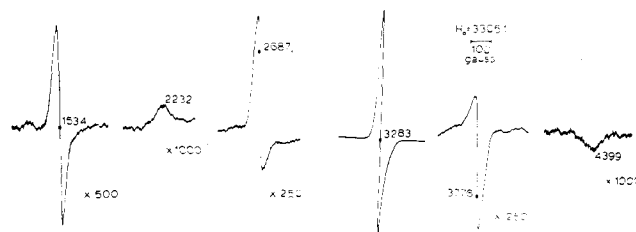


Figure 1. ESR spectrum of $\text{C}_6\text{Cl}_6^{2+}$ obtained by irradiation of a solution of HCB in $\text{SbF}_5\text{-Cl}_2$.

triplet state⁷ (I) appeared within a few minutes. The species responsible for the triplet spectrum was stable indefinitely below 77°K but disappeared after a few minutes at 196°K. The signal intensity was proportional to $1/T$, indicating a ground state triplet or a species within a few calories/mole of the ground state. From the spectrum we determined the zero-field parameters⁷ which measure the magnetic dipole interaction of the two unpaired electrons: $D_I = 0.1012 \pm 0.0001 \text{ cm}^{-1}$ and $E_I < 0.0003 \text{ cm}^{-1}$; $g_{xy} = 2.0192$, $g = 1.9961$. We suggest that these data are best accommodated by the dipositive ion I. For comparison $D_{\text{IIB}} = 0.1445 \text{ cm}^{-1}$, $E_{\text{IIB}} < 0.0003 \text{ cm}^{-1}$, $g_{xy} = 2.0112$, and $g_z = 1.9986$.^{8,9} A second ground-state triplet with parameters similar to those of IIB was observed on prolonged irradiation, particularly with $\lambda < 3100 \text{ \AA}$. Presumably a CCl fragment is lost producing IIB from I or a precursor of I.⁹

E indicates the deviation of the triplet from threefold or higher symmetry. The apparent zero value of E_I is compatible with the sixfold symmetry that might be expected from a benzene dipositive ion.

$$D \propto (3z^2 - r^2)/r^5$$

where r is the distance between the unpaired electrons and z the component of that distance along the axis perpendicular to the molecular plane. We use D_{IIB} to estimate D_I . We assume that the geometrical factors in the interaction between the unpaired spin densities on C-Cl fragments which are "ortho" or "meta" are the same in I and IIB. A justification for this approach is that most of the spin density is on carbon and the interactions will not be greatly affected by the changes in the CCl angle between I and IIB. Then the difference in zero-field parameters for I and IIB is due chiefly to the increased spin density on the atoms of IIB because of the smaller ring size. The spin density on a C-Cl fragment of I is five-sixths as large as that on IIB and, as D is proportional to the product of spin densities, $D_{\text{I(ealed)}} = (5/6)^2 D_{\text{IIB}}$. The "para" interaction which is found only in I will yield an increase of $\sim 4\%$. We then find that $D_{\text{I(ealed)}} = 0.104 \text{ cm}^{-1}$ in good agreement with that observed. The calculated value of D_I should be an upper limit as the dipositive charge in I will place more net charge and spin on chlorine than the monopositive charge in IIB.

Additional support for the assignment of the triplet spectrum to I arises from a comparison of the g factors for I and IIB, particularly g_{xy} . The substantial devi-

(7) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(8) R. S. Hutton, unpublished results.

(9) An analogous $\text{C}_5 \rightarrow \text{C}_3$ transformation has yielded neutral C_3H_3 .² Also G. Porter and B. Ward, *Proc. Roy. Soc., Ser. A*, **303**, 139 (1968).

ation from the free spin value of $g_e = 2.0023$ is in agreement with the presence of heavy nuclei in both. The similar electron configurations of I and IIb imply that a major factor in the larger deviations of g_I from g_e is the smaller energy gaps to excited states in the larger ring system of I [(A) and (B)]. The magnitudes of the g shifts are inversely proportional to such energies.¹⁰ The major contributors to the Δg_{xy} are probably states in which in-plane nonbonding electrons on chlorine are transferred to the partially vacant π -orbitals.

The metastable triplet state of the parent HCB has $D = 0.154 \text{ cm}^{-1}$.¹¹ To a good approximation the spin density should be evenly distributed around the ring ($E = 0.0015 \text{ cm}^{-1}$).¹¹ The larger D implies that there is more spin in the ring of the neutral molecule than in I. Thus the molecular orbitals occupied by the unpaired electrons in I include chlorine atomic orbitals and our statement of four π -electrons is only approximate.

There is additional support for this conclusion that the driving force for chlorine π -electrons to enter the ring is delocalization of the positive charge. For the metastable triplet state of benzene, where the net charge is absent, $D = 0.157 \text{ cm}^{-1}$,¹² almost the same as that of the neutral hexachlorobenzene. In the C_6^+ systems, $D_{IIa} = 0.185 \text{ cm}^{-1}$ while $D_{IIb} = 0.144 \text{ cm}^{-1}$, again indicating movement of spin out of the ring as the positive charge is stabilized by chlorine.

In view of the decrease of D with chlorine substitution in a positively charged system, it is likely that $C_6H_6^{2+}$ will have $D = 0.14\text{--}0.15 \text{ cm}^{-1}$, similar to that of the phosphorescent triplet with little charge and spin delocalization into the C-H bonds.

(10) S. H. Glarum, *J. Chem. Phys.*, **39**, 3141 (1963). The spin-orbit contribution to g implies a contribution to D as well.

(11) M. A. El-Sayed, A. A. Gwaiz, and C. T. Lin, *Chem. Phys. Lett.*, **16**, 281 (1972).

(12) M. S. de Groot, I. A. M. Hesselman, and J. H. van der Waals, *Mol. Phys.*, **13**, 583 (1967).

(13) Bell Laboratories.

(14) Rutgers University.

E. Wasserman,^{*13,14} R. S. Hutton¹³
V. J. Kuck,¹³ E. A. Chandross¹³

Bell Telephone Laboratories
Murray Hill, New Jersey 07974
School of Chemistry, Rutgers University
New Brunswick, New Jersey 08903

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Reductive Rearrangement of 5,6:7,8-Bis(dichloromethano)octamethyl-5,6,7,8-tetrahydronaphthalene by Sodium Naphthalene. Evidence of a Carbene Intermediate

Sir:

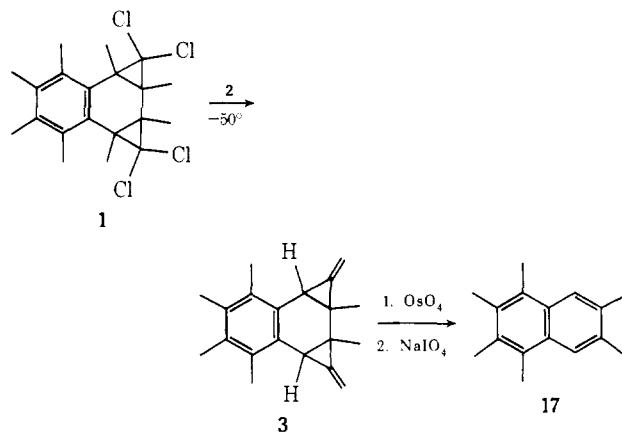
The recent report,¹ proposing a carbene intermediate for the reaction of geminate alkyl dihalide with sodium naphthalene, seems to have revealed a new aspect of the reduction of organic halides with naphthalene radical anion.² In relation to this finding, the authors herein present the first evidence of substituent shift to a neighboring cyclopropylidene center which is generated from the *gem*-dichlorocyclopropane function as illustrated by the reduction of compound **1**³ with sodium naph-

(1) G. D. Sargent, C. M. Tarum, Jr., and S. M. Kastner, *J. Amer. Chem. Soc.*, **94**, 7174 (1972).

(2) For example, see J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).

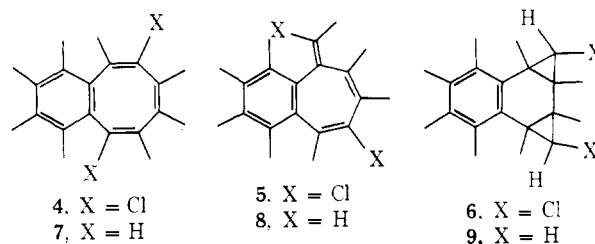
thalene (**2**). In this reaction, but at higher temperatures, is also observed a novel skeletal anionic rearrangement of the tricyclo[5.1.0.0^{2,4}]octene system.

Treatment of **1** in THF at below -50° with 4 equiv of **2** afforded a product mixture consisting mainly of compound **3**, 75%, mp 99° . The mass spectrum of **3** showed its parent ion peak at m/e 264 ($C_{20}H_{24}$), indicative of four chlorine atoms abstracted from **1** without hydrogen substitution. The nmr spectrum indicates a symmetric structure of **3** by the signals appearing at τ 8.59 (6 H, s), 7.85 (2 H, q, $J = 2.0$ and 2.5 Hz), 7.80 (6 H, s), 7.70 (6 H, s), 4.75 (2 H, d, $J = 2.0$ Hz), and 4.58 (2 H, d, $J = 2.5$ Hz). The uv spectrum is similar to that of **1**.⁴ The oxidation of **3** with osmium tetroxide in pyridine followed by successive treatment with sodium metaperiodate in methanol yielded 1,2,3,4,6,7-hexamethylnaphthalene (**17**), 20%. Since the isomeri-



zation of 1,2,3,4,5,8-hexamethylnaphthalene to **17**⁵ did not take place under the same oxidation condition, product **3** was assigned to 5,6:7,8-bis(ethylideno)-1,2,3,4,6,7-hexamethyl-5,6,7,8-tetrahydronaphthalene.

On the other hand, reduction of **1** at 25° in THF yielded a mixture of complex components different from that at -50° . The isolated products were **4**, **5**, and **6** and their corresponding hydrocarbons **7**, **8**, and **9**, but **3** was not detected.⁶ The change of the product composition *vs.* the amount of the reductant added was analyzed by gc and mass spectral measurements, in which a Cl_3 and two Cl_2 compounds appeared simultaneously as compound **1** was consumed, and these Cl_2 compounds were gradually reduced to hydrocarbons **7** and **8** *via* some Cl_1 compounds. The structure determination of the products **4**–**9** was achieved by means of



(3) For the addition of CBr_2 , see H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972).

(4) λ_{max} (cyclohexane): **1**, 223 nm ($\log \epsilon$ 4.54), 288 (2.48); **3**, 220 (4.34), 280 (2.60).

(5) Unpublished results. Acid-catalyzed isomerization of 1,2,3,4,5,8-hexamethylnaphthalene into **17** *via* 1,2,3,4,5,7-hexamethyl isomer takes place quantitatively in such strong acidic media as CF_3COOH or $HCl-ZnCl_2$.

(6) Yields attained after the addition of 6 equiv mol of **2** were 55, 35, and 7% for **7**, **8**, and **9**, respectively.