(46) P. Pulay, *Mol. Phys.*, **17**, 197 (1969); P. Pulay and W. Meyer, *J. Mol. Spectrosc.*, **40**, 59 (1971).
(47) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 5968 (1975).
(48) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
(49) B. S. Rabinsovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1965).
(50) G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, McGraw-Hill, New York, N.Y., 1950.
(51) Unpublished work in these laboratories.
(52) M. J. S. Dewar, R. C. Haddon, W.-K. Li, W. Thiel, and P. K. Weiner, *J. Am. Chem. Soc.*, **97**, 4540 (1975).

Ground States of Molecules. 43.[1] A MINDO/3 Study of the Rearrangement of Phenylcarbene to Cycloheptatrienacarbene

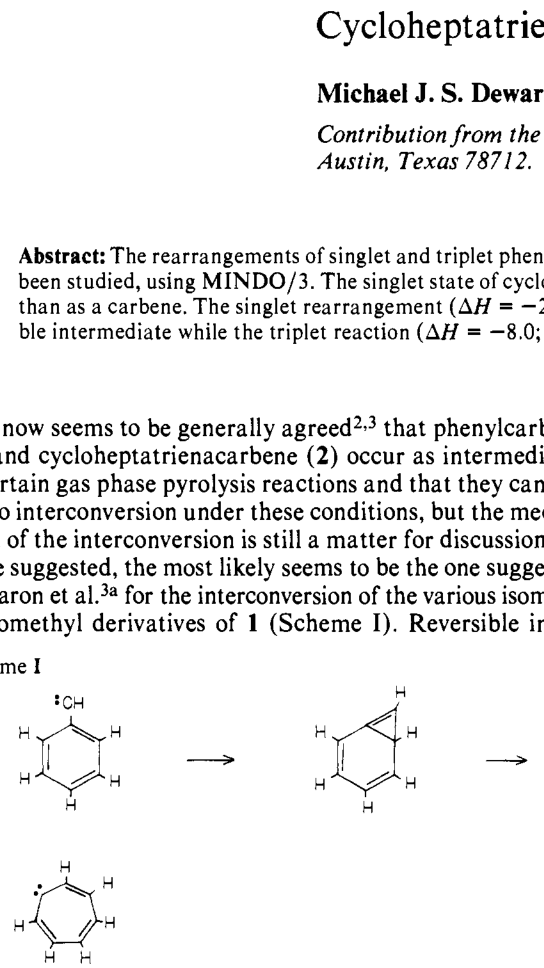
Michael J. S. Dewar* and D. Landman

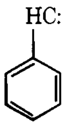
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received December 9, 1976*

Abstract: The rearrangements of singlet and triplet phenylcarbene to the corresponding states of cycloheptatrienacarbene have been studied, using MINDO/3. The singlet state of cycloheptatrienacarbene is better represented as a standard cyclic tetraene than as a carbene. The singlet rearrangement ($\Delta H = -26.8$; $\Delta E^{\ddagger} = 6.3$ kcal/mol) involves bicyclo[4.1.0]heptatriene as a stable intermediate while the triplet reaction ($\Delta H = -8.0$; $\Delta E^{\ddagger} \geqslant 18.5$ kcal/mol) takes place in a single step.

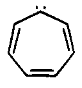
It now seems to be generally agreed[2,3] that phenylcarbene (**1**) and cycloheptatrienacarbene (**2**) occur as intermediates in certain gas phase pyrolysis reactions and that they can undergo interconversion under these conditions, but the mechanism of the interconversion is still a matter for discussion. Of those suggested, the most likely seems to be the one suggested by Baron et al.[3a] for the interconversion of the various isomeric monomethyl derivatives of **1** (Scheme I). Reversible interconversion of **1** and **2** by this mechanism should lead to scrambling of the six methine groups, without scrambling the methine and carbenoid carbon atoms. Hedaya et al.[3b] have shown by ^{13}C labeling that this is indeed the case, at temperatures below 600 °C.

Scheme I



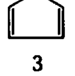


1

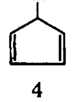


2

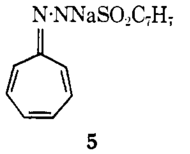
At higher temperatures, **1** undergoes ring contraction[3d,e] to fulvenallene (**3**) and 2-ethinylcyclopentadiene (**4**), and Crow and Paddon-Row[3c] have shown by ^{13}C labeling that hydrogen shifts occur in the conversion of **1** to **3** above 770 °C. However, the carbene interconversion (Scheme I), leading to ring expansion of **1**, appears to be faster than either the hydrogen shift or the ring contraction, even at the higher temperatures.



3



4



5

When **2** was generated in the gas phase by heating the sodium salt (**5**) of the tosylhydrazone of tropone, under conditions which led to the conversion of **1** to **3**, it was found that no ring contraction occurred. Crow and Paddon-Row[3c] have suggested that the **2** formed from **5** may be in a different electronic state from that formed from **1**, on the basis of MO calculations which predicted the singlet and triplet forms of **2** to be very similar in energy.

We recently reported[5] a MINDO/3[6] study of the conversion of benzyl cation (**6**) to tropylium ion (**7**) which led to apparently satisfactory conclusions. Since **1** and **2** are conjugate bases of **6** and **7**, respectively, and since MINDO/3 has been shown[7] to give good results for singlet and triplet carbene, we decided to use it to study the conversion of **1** to **2.**

Procedure

The calculations were carried out using the standard MINDO/3 procedure[6] together with the associated DFP geometry program.[6] Minimum energy reaction paths (MERP) were found by the usual reaction coordinate method.[7] The transition states located approximately in this way were refined by minimizing the scalar gradient of the energy.[8,9] Each stationary point located in this way on the potential surface was shown to be a true saddle point by calculating the corresponding Hessian (second derivative) matrix and establishing that it had one, and only one, negative eigenvalue.[8,9] Triplet surfaces were calculated using a spin-unrestricted version of MINDO/3 (UMINDO/3) in preference to the "half-electron" (HE) method for reasons stated in an earlier paper.[5] Studies of numerous open-shell systems have shown that both procedures lead to similar results.[11]

Results and Discussion

The geometries, heats of formation, and distributions of formal charge calculated for singlet **1** and singlet **2** are shown in Figure 1a–d.

The geometry of **1** differs in an interesting way from that calculated[5] for **6.** Both molecules are planar, but whereas the C_1–C_7 bond in **6** was very short (1.37 Å), corresponding to a

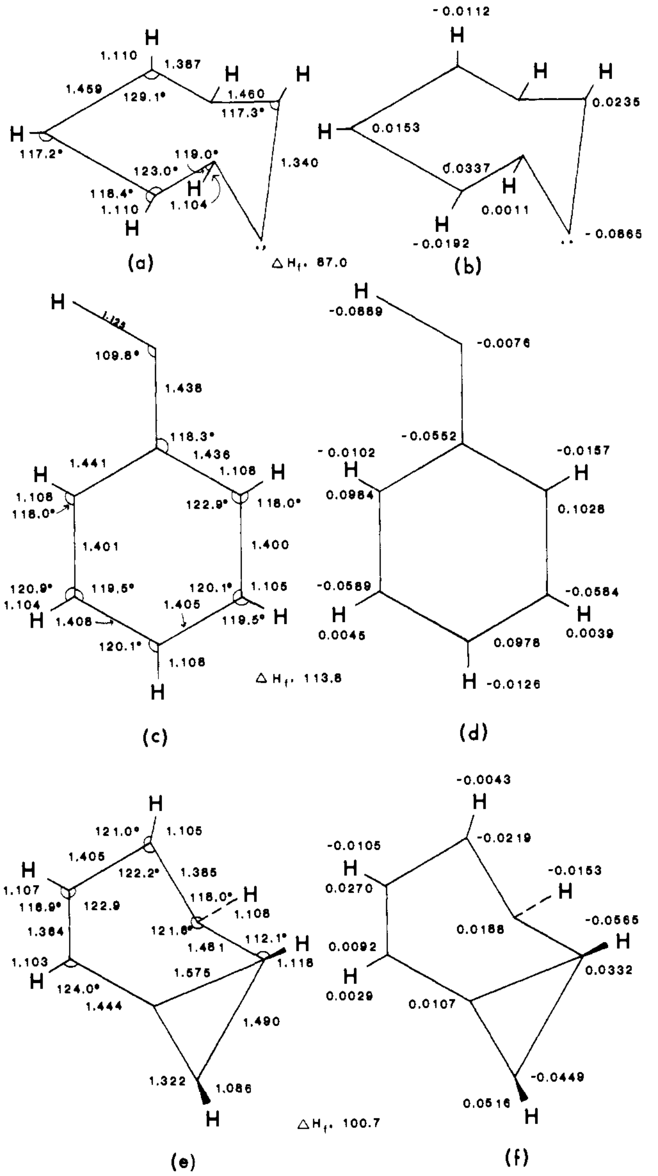
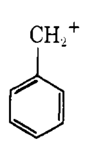
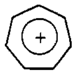


Figure 1. Geometries (bond lengths in Å) and distributions of formal charge (in units of the electronic charge) for singlet carbenes: (a), (b) cycloheptatrienacarbene (**1**); (c), (d) phenylcarbene (**2**); (e), (f) bicycloheptatrienacarbene (**10**).

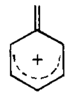


6



7

structure best represented by **8**, that in **1** is little shorter than the usual "polyene" C-C bond length, implying only a small resonance interaction between the phenyl group and the carbenoid center. This of course is not surprising, because while such an interaction in **6** can arise only at the expense of charge separation, in **1** it leads only to a redistribution of the formal positive charge. This conclusion is supported by the very small formal negative charge at C_7 in **1**. Note incidentally the quite significant difference between the formal charges at the adjacent ortho positions, one cis and the other trans to the exocyclic hydrogen. The HOMO of **1** corresponds, as expected, to a σ-type MO strongly localized on the exocyclic carbon atom.



8

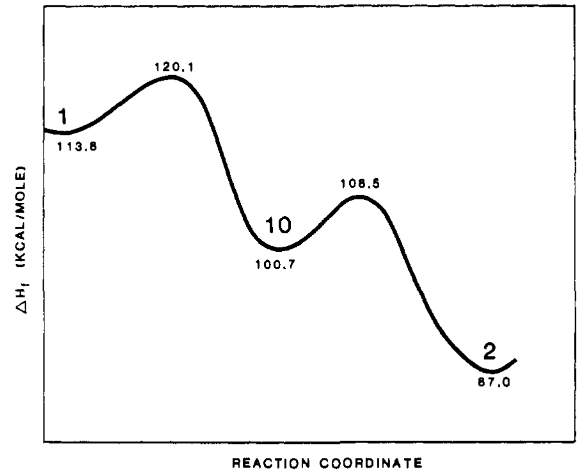
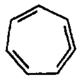


Figure 2. Minimum energy reaction path (MERP) for conversions of **1** to **2** via **10**.

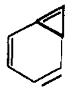
A similar argument would lead one to expect **2** to be much less aromatic than **7**. Our calculations indeed predict their structures to be quite different, **7** having D_{7h} symmetry[5] while **2** has a nonplanar structure with alternating bonds. Indeed, examination of the calculated structure indicates that the molecule should be regarded not as a carbene but rather as a strained cyclic polyene, i.e., cycloheptatetraene (**9**). The lengths of the bonds are all close to values found in classical polyenes and while the allenic CC bonds are longer than those in allene itself (1.308 Å[12]), this is not surprising in view of the distortion of the allene moiety in **9** from the normal allene geometry.



9

The heat of reaction calculated for **1** → **2** (−26.8 kcal/mol) is very close to the corresponding[5] value for **6** → **7** (−24.8 kcal/mol). However, while the heat of formation calculated[5] for **6** agreed quite well with experiment, being too positive by 4.4 kcal/mol, that for **7** was too negative by 14.4 kcal/mol. While part of this discrepancy could be due to uncertainties in the experimental value for the ionization potential of the tropyl radical (cf. ref 5), it seems clear that the calculated heat of reaction for **6** → **7** is too negative. If so, the MINDO/3 value for **1** → **2** may also be too negative. There is, however, little doubt that the reaction must be exothermic, the equilibrium between **1** and **2** favoring the latter.

Figure 2 indicates the form of the MERP for **1** → **2**. It will be seen that bicyclo[4.1.0]heptatriene (**10**) is formed as a stable intermediate, whose calculated heat of formation indeed implies it to be more stable by 13 kcal/mol than **1**. However, as in the case of the similar intermediate involved in the conversion of **6** to **7**, this may be an artifact, due to the known[6] tendency of MINDO/3 to overestimate the stability of three-membered rings. Comparison with results for analogous compounds suggests that the error in the case of **10** probably amounts to ca 10-15 kcal/mol, its formation from **1** therefore being in reality more or less thermoneutral.



10

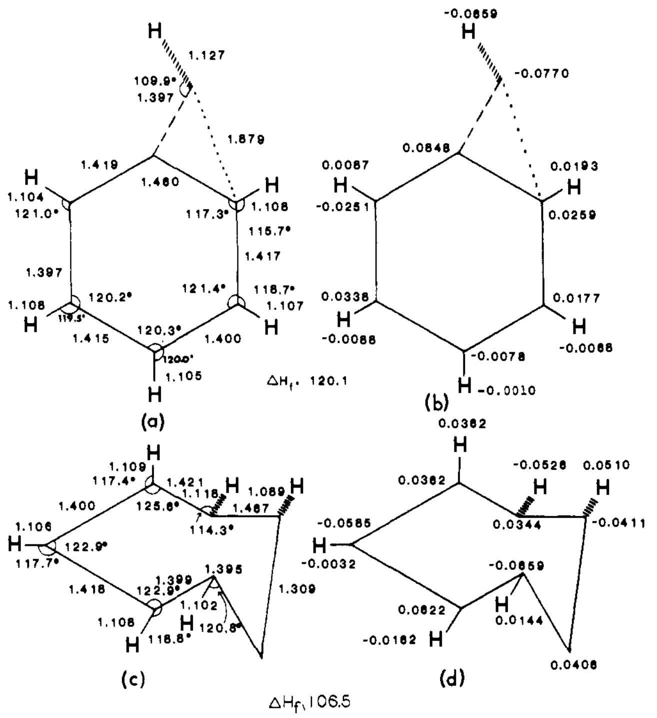


Figure 3. Geometries (bond lengths in Å) and distributions of formal charge (in units of the electronic charge) for transition states: (a), (b) **1** → **10**; (c), (d) **10** → **2**.

The calculated geometry, heat of formation, and distribution of formal charge calculated for **10** are shown in Figures 1e and 1f while Figures 3a and 3b show similar results for the transition state for formation of **10** from **1**. It will be seen that the transition state is nearer to the reactant (**1**) than the product (**10**) in structure. The exocyclic hydrogen in **1** has bent out of the plane of the ring in the transition state, allowing delocalization of the carbenoid lone pair. This is reflected by the decrease in the C_1C_7 bond length (from 1.436 to 1.397 Å) and by the form of the HOMO, which is no longer strongly localized on C_7. The bond that is being formed (C_2-C_7) is still long (1.879 Å). The form of the HOMO indicates that it is being formed by a π-type interaction between the carbenoid lone-pair electrons and the π electrons of the ring.

Figures 3c and 3d show the geometry, heat of formation, and distribution of formal charge calculated for the transition state for **10** → **2**. This resembles the intermediate **10** in structure and its calculated heat of formation is therefore also probably somewhat too negative. In spite of these uncertainties, however, it seems fairly clear that the transition state for the overall conversion of **1** to **2** corresponds to that for the first step, i.e., **1** → **10**. The corresponding activation energy is only 6.3 kcal/mol so this reaction would be extremely fast under the conditions of a flash vacuum pyrolysis. The activation energy of the reverse reaction, **2** → **1**, is of course much greater, 33 kcal/mol. While this value may be too high for the reasons indicated above, it still corresponds to a very high rate of reaction at 600 °C (first order rate constant, $\sim 6 \times 10^4\ s^{-1}$). Our results are therefore consistent with the experimental evidence, that the equilibrium **1** $\rightleftharpoons$ **2** is established under the conditions of a flash vacuum pyrolysis at 600 °C, assuming that the reactions take place in the singlet manifold.

The geometries, heats of formation, and distributions of formal charge calculated for triplet **1** and triplet **2** are shown in Figure 4a-d. In triplet **1**, the calculated HCC bond angle at the carbene center (142.9°) is in reasonable agreement with the value (155°) estimated from the ESR spectrum.[13,14]

Just as singlet **1** is derived from benzyl anion by loss of a proton, so likewise is triplet **1** derived from benzyl radical by loss of a neutral hydrogen atom. In the former case, the loss of a proton leads to a perturbation of the π system, due to the increased formal charge at the exocyclic carbon atom. In the latter, however, the π system should remain essentially unchanged. The bond lengths calculated for triplet **1** conform to this expectation, corresponding to a structure best represented by **11** (cf. **8** for benzyl cation).

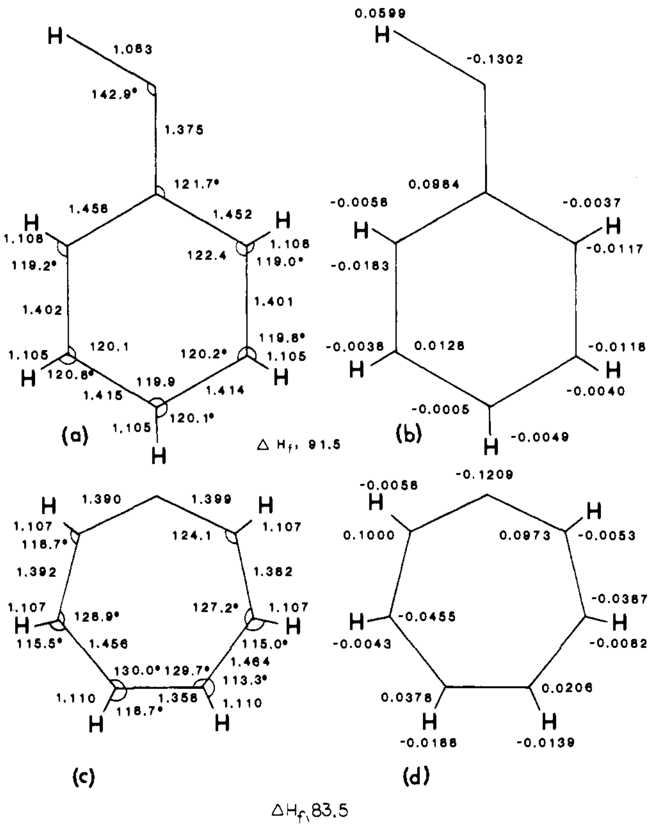
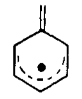


Figure 4. Geometries (bond lengths in Å) and distributions of formal charge (in units of the electronic charge) for triplet carbenes: (a), (b) phenylcarbene (**1**); (c), (d) cycloheptatrienacarbene (**2**).



11

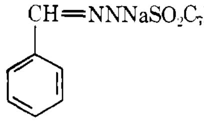
Triplet **2** should likewise have a geometry similar to that of the tropyl radical, and this is also the case. Both systems are planar and both show similar bond alternation. In the case of tropyl radical, the departure from D_{7h} symmetry is of course due to the Jahn-Teller effect, the unpaired electron occupying one of two π MO's which are degenerate if the system has D_{7h} symmetry.

The heat of formation calculated for triplet **1** is less than that for the singlet by 22.3 kcal/mol, much more than the singlet-triplet separation calculated by MINDO/3 for carbene itself (8.7 kcal/mol[7]). The separation should be greater in the case of **1** because the resonance interaction between the ring and the exocyclic methine group is greater in the triplet than in the singlet (see above). However, since the separation in CH_2 now seems to be larger than the MINDO/3 value (19.5 kcal/mol[15]), it seems likely that the same will also be true for **1**. Assuming that the MINDO/3 value for the difference between the two singlet-triplet separations is correct, that for **1** would then be 33 kcal/mol.

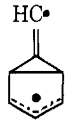
Similar arguments should apply in the case of **2** but here the singlet-triplet separation calculated by MINDO/3 (3.5 kcal/mol) is much *less* than that for carbene itself. This difference between **1** and **2** is of course due to the fact that singlet **2** succeeds in stabilizing itself in a manner not available to the tropyl radical, i.e., by valence tautomerism to cycloheptatetraene (**9**).

A preliminary search of the triplet potential surface showed that the conversion of **1** to **2** does not take place via triplet **10.** The transition state was not located precisely but its heat of formation was found to be close to, and not less than, 120 kcal/mol, corresponding to an activation energy of 18.5 kcal/mol and a reverse (**2** → **1**) activation energy of 26.5 kcal/mol. Such reactions would again take place very rapidly at 600 °C.

As noted above, **2,** when generated directly from the sodium salt of tropone tosylhydrazone (**5**), apparently fails[3e] to give the ring-contracted isomers **3** and **4** under conditions where these are formed[3c] by similar pyrolysis of the sodium salt of benzaldehyde tosylhydrazone (**12**). Crow and Paddon-Row[3c] suggested that this difference might be due to the reactions taking place on surfaces of different multiplicity. If, as has been suggested,[3b] the conversion of **1** to **4** and **5** occurs via the biradical intermediate **13,** it is easily seen that this process could be very much easier on the singlet manifold because the difference in energy between the singlet and triplet forms of **14** must be quite small whereas that between singlet and triplet **1** is very large (33 kcal/mol according to MINDO/3). This explanation, however, depends on the assumption that while pyrolysis of **12** gives singlet **1,** pyrolysis of **5** gives triplet **2.** One would also have to assume that intersystem crossing between the singlet and triplet surfaces is slow on the time scale of a flash vacuum pyrolysis. These postulates seem rather difficult to justify.



12



13

Further work is clearly needed to clarify the reactions taking place in this very interesting system and such studies are in progress.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant No. AFOSR-75-2749) and the Robert A. Welch Foundation (Grant No.F-126). The calculations were carried out using the CDC 6400-6600 computer at The University of Texas Computation Center. One of us (D.L.) acknowledges the award of a Robert A. Welch Postdoctoral Fellowship.

References and Notes

(1) Part 42: M. J. S. Dewar and H. S. Rzepa, *J. Mol. Struct.*, submitted.
(2) For general references, see M. J. Jones, Jr., *Acc. Chem. Res.*, 7, 415 (1974).
(3) (a) W. J. Baron, M. Jones, and P. P. Gaspar, *J. Am. Chem. Soc.*, **92,** 4739 (1970); (b) E. Hedaya and M. E. Kent, *ibid.*, **93,** 3283 (1971); (c) W. D. Crow and M. N. Paddon-Row, *ibid.*, **94,** 4746 (1972); (d) P. O. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *ibid.*, **92,** 2147 (1970); (e) C. Wentrup and K. Wilezek, *Helv. Chim. Acta*, **53,** 1459 (1970).
(4) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90,** 5457 (1968).
(5) C. Cone, M. J. S. Dewar, and D. Landman, *J. Am. Chem. Soc.*, **99,** 372 (1977).
(6) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1285, 1294, 1302, 1307 (1975).
(7) M. J. S. Dewar, R. C. Haddon, W. K. Ii, W. Thiel, and P. K. Weiner, *J. Am. Chem. Soc.*, **97,** 4540 (1975).
(8) J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, **94,** 2625 (1972); **95,** 4512 (1973).
(9) Using a program written by Dr. P. K. Weiner.
(10) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22,** 571 (1954).
(11) M. J. S. Dewar, A. Komornicki, D. Landman, S. H. Suck, and P. K. Weiner, unpublished work.
(12) A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17,** 136 (1965).
(13) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40,** 2408 (1964).
(14) Gleiter and Hoffmann also calculated (EH) this angle to be 143°. They gave arguments for believing that the experimental[13] value may be too large.
(15) P. F. Zittel, G. B. Ellison, S. V. O. Neill, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98,** 3731 (1976).

Xα Multiple Scattering Calculations on Copper Porphine[1a]

David A. Case[1b] and Martin Karplus*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received January 21, 1977*

Abstract: Spin-restricted and -unrestricted Xα calculations on copper porphine are performed and the results are compared with other calculations (EH, PPP) and the available experimental information; the latter include the redox properties, electronic spectra of the neutral species, the anion, and the cation, and high-resolution crystal ESR data. The relation of Xα eigenvalues to Hartree–Fock orbital energies is discussed. The ground state is formally Cu^{2+} (d^9), but formation of a d^{10} complex by reduction or charge-transfer excitation is predicted to occur at low energy. Some experimental evidence supports this prediction, although it is in disagreement with other calculations. Comparison of the charge distributions obtained by different calculations shows general agreement though there are some important differences. The effect of spin polarization on the orbital energies and coefficients is found to be small but not negligible. Perturbation theory is used to investigate the ESR spectrum. The calculated g values and hyperfine tensors are found to be in good agreement with experiment; an exception is the Fermi contact coupling, whose calculated value is too small by 35%. The ligand field description of ESR data is analyzed and it is shown that for copper porphyrin the conventional treatment yields qualitatively correct results but has quantitative deficiencies; the latter include neglect of charge-transfer excited states and the assumption of a single radial function for all copper 3d orbitals.

(I) Introduction

Metalloporphyrins have been prepared with most of the atoms of the first transition series.[2a] They have been intensively studied, both for their intrinsic interest and because of their biological importance. For the copper porphyrins, which correspond to a (Cu^{2+}, d^9) configuration, detailed high-resolution electron-spin resonance spectra are available.[2b] Additional data are provided by studies of the optical[3] and photoelectron spectra.[4] The interpretation of these results is simplified by the