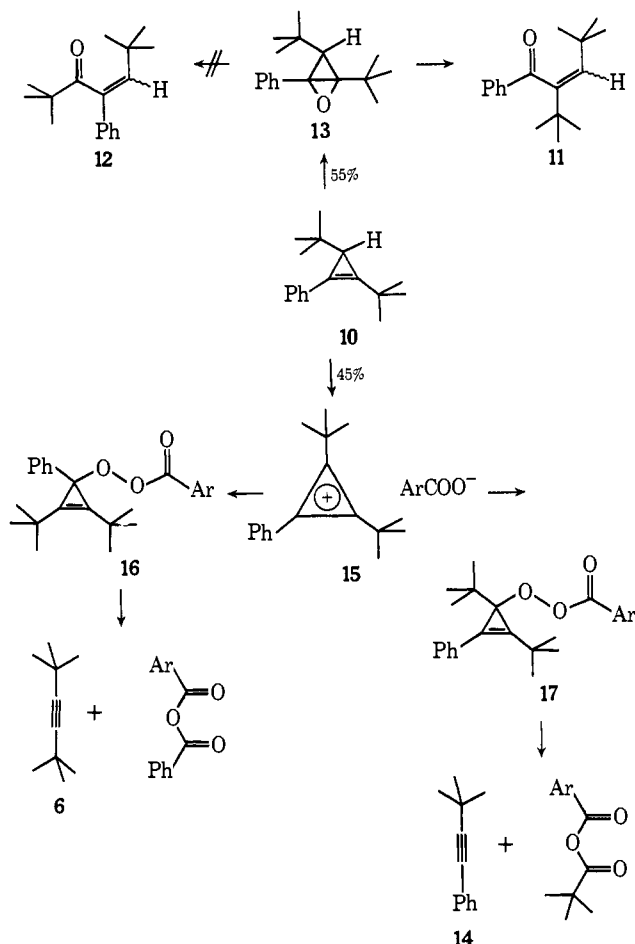**Scheme II.** MCPBA Oxidation of **10**

11. These results support the intermediacy of peroxy esters **16** and **17** in the formation of acetylenes **6** and **14**, respectively, and exclude **16** as a possible precursor to **11** in the peroxy acid oxidation of **10**. In accordance with the proposed mechanism, oxidation of cyclopropene **18**[6] afforded only epoxy ketone **20**,[10] mp 123–124°, the structure of which (exclusive of stereochemistry) was established on the basis of the following spectral data: ir (ν_{max} CCl$_4$) 1690 cm^{-1}; uv (λ_{max}, 95% EtOH) 249 mμ (ϵ 11,600); nmr (CCl$_4$, δ) 0.83 (9 H, s), 1.00 (9 H, s), 1.57 (3 H, s), 7.20–7.45 (3 H, m), 7.70–7.95 (2 H, m); mass spectrum m/e 274, 105 (base peak).
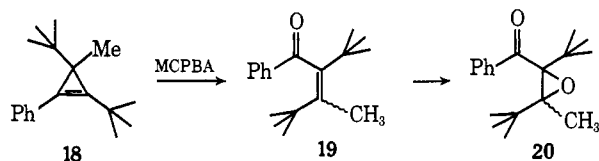
The reaction of **5** with MCPBA was unaffected by the presence of the radical scavengers bromotrichloromethane or β,β-dichlorostyrene precluding a mechanism involving radical abstraction of hydrogen as a first step in the formation of the tri-*tert*-butylcyclopropenyl cation **8**. Thus the process appears to involve a direct transfer of hydride from the 3 position of the cyclopropene to the terminal electrophilic oxygen of MCPBA to generate a cyclopropenyl cation as the *m*-chlorobenzoate salt. To our knowledge this is the first ex-

(10) Epoxy ketone **20** undoubtedly arises from epoxidation of α,β-unsaturated ketone **19**.

ample of the direct oxidation of a hydrocarbon to a carbonium ion by a peroxy acid.

The instability of peroxy esters **9**, **16**, and **17** is not surprising in view of the fact that the peroxide intermediates proposed in the oxidative decarbonylation of cyclopropenones[11] and cyclopropanones[12] with MCPBA and hydrogen peroxide, respectively, were not isolated under the reaction conditions. Furthermore, DePuy has observed that the related nitrite esters of cyclopropanols are extremely unstable, even at −50°.[13] The low activation energy for the decomposition of these three-membered ring nitrites and peroxides probably reflects (at least in part) a relief of ring strain in the transition state by partial ring opening as previously suggested.[13]

In theory, the decomposition of these peroxy esters may proceed *via* a radical, ionic, or concerted process.[14] If a radical or ionic mechanism is operative, it must be intramolecular (*i.e.*, radical cage or ion pair) since radical scavengers had no significant effect on the reaction of **5** with MCPBA and the reaction of **8** (perchlorate salt) with MCPBA in the presence of sodium acetate resulted in no incorporation of acetate into the anhydride product. Further mechanistic studies are in progress.

(11) J. K. Crandall and W. W. Conover II, *Tetrahedron Lett.*, 583 (1971).
(12) J. E. Baldwin and J. H. I. Cardellia, *Chem. Commun.*, 588 (1968).
(13) C. H. DePuy, *Accounts Chem. Res.*, 1, 33 (1968).
(14) For reviews of peroxide reactions see (a) D. Swern, Ed., "Organic Peroxides," Vol. 1, Wiley-Interscience, New York, N. Y., 1970; (b) Ya. K. Syrkin and I. I. Moiseev, *Russ. Chem. Rev.*, 29, 193 (1960); (c) J. B. Lee and B. C. Uff, *Quart. Rev., Chem. Soc.*, 21, 429 (1967).

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Transmission of π Interactions through σ Bonds in Tricyclo[4.4.2.0^{1,6}]dodeca-3,8-diene-11,12-dione and Its Tetrahydro Derivative

Sir:

The unusual spectral properties of the title compounds in the visible region have been reported and discussed by Bloomfield and Moser.[1] In an effort to investigate the electronic structure of these systems we have determined the molecular structure of the diene[2] and performed some molecular orbital calculations.[3] The results of these investigations lead to interesting conclusions regarding the nature of the π-electron system interactions involved.

The diene compound is found to crystallize in the monoclinic space group $P2_1/c$ with $a = 7.438$, $b = 11.539$, $c = 12.935$ Å, and $\beta = 116.22°$. There are four molecules per unit cell. The structure refined to a final R index of 0.065 for 1870 independent X-ray reflections.

(1) J. J. Bloomfield and R. E. Moser, *J. Amer. Chem. Soc.*, 90, 5625 (1968).
(2) R. Fink, D. van der Helm, and S. C. Neely, Abstracts, American Crystallographic Association Meeting, March 1969, p 34.
(3) S. C. Neely, R. Fink, and D. van der Helm, Abstracts, Southeastern–Southwestern Regional Meeting of the American Chemical Society, Dec 1970, p 168.
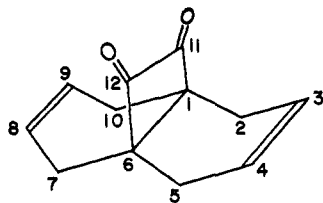
Figure 1. Configuration of the diene in the molecular crystal. The symmetry is approximately C_{2v}.

The configuration of the molecule is of particular interest since the Bloomfield and Moser rationale of the spectra depended upon the conformations of the six-membered rings. In the crystal the molecule has the two six-membered rings in the boat form and has approximate C_{2v} symmetry as depicted in Figure 1. The largest deviation from C_{2v} symmetry is 0.065 Å for the oxygen bonded to C_{12}.

The goal of the MO calculations was to explain the positions of the n → π* spectral bands appearing in the visible spectra of the title compounds. The diene exhibits a band with λ_{max} 538 nm while the tetrahydro derivative has λ_{max} 461 nm. Specifically, it was anticipated that the interactions between the double bonds in the six-membered rings of the diene with the dione system should be the predominant factor affecting the observed band differences.

The first MO models consisted of the dione π system interacting with two appropriately situated ethylenes representing the diene π system, since interspatial interaction of these systems had been suggested by Bloomfield and Moser. The resulting states, however, indicated that the diene should absorb at shorter wavelengths than the tetrahydro derivative. This conclusion is in qualitative disagreement with experiment. Different MO approaches using the same model (Hückel,[4] extended Hückel,[5] SCF-CI,[6] and CNDO/2[7]) changed the energies but not the erroneous qualitative ordering. These results clearly contradict the plausibility of the interspatial interaction model.

Careful examination of the diene structure reveals that the p_π AO of C_{11} has apparently significant overlap with the $sp_\sigma{}^3$ AO of C_1 directed along the C_1-C_2 or C_1-C_{10} bonds. By symmetry the p_π AO of C_{12} has equivalent overlaps with $sp_\sigma{}^3$ AO's on C_6. Furthermore, there appears to be significant overlap of a p_π AO on C_3 with the $sp_\sigma{}^3$ AO on C_2 directed along the C_2-C_1 bond, etc. Some of the overlaps of interest were calculated[8] and are listed: $S_{1,11}(sp_\sigma{}^3, p_\pi) = 0.140$; $S_{2,3}(sp_\sigma{}^3, p_\pi) = 0.103$; $S_{3,11}(p_\pi, p_\pi) = 0.036$. These confirm that indeed the overlaps in question are three-four times greater than the overlap of the p_π AO's on C_3 and C_{11} and the symmetry-related pairs.

(4) Matrix Diagonalization program furnished by Mr. Carl C. Zinsser, Department of Chemistry, University of Oklahoma, Norman, Okla. 73069.

(5) R. Hoffmann, J. Chem. Phys., 39, 1397 (1963) (program by E. B. Morre, W. C. Cook, and A. R. M. Rom, QCPE program 64, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.).

(6) J. E. Bloor, P. N. Daykin, and P. Boltwood, Can. J. Chem., 42, 121 (1964); J. E. Bloor and N. Brearley, ibid., 43, 1761 (1965) (program by J. E. Blood and B. R. Gilson, QCPE program 71.2).

(7) J. Del Bene and H. H. Jaffé, J. Chem. Phys., 48, 1807 (1968) (program furnished by Dr. H. H. Jaffé; QCPE program 174 is a recently available modified version).

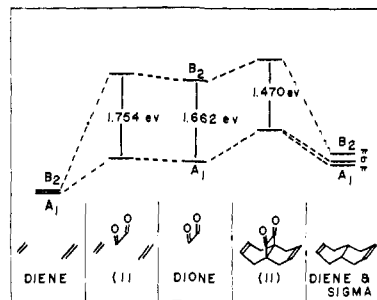(8) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys., 17, 1248 (1949).

Figure 2. The effect on the n → π* transition energy of the dione system due to interaction with the diene system. I incorporates through-space interaction of the π systems with the σ network omitted. II includes all valence electrons.

Thus, it is evident that the σ bonds should be included in a valid MO treatment. Accordingly, the extended Hückel method[5] was applied with the inclusion of all π and σ valence electrons. The results are in qualitative agreement with the experimental ordering of the transitions, but the calculated wavelengths of 843 and 770 nm are much too long.

The results of these calculations are summarized in Figure 2. The A and B labels are the conventional irreducible representations of the C_{2v} point group. The A_1 levels shown for the dione and for I and II are nonbonding (n) MO's and in each case were found to be the highest occupied MO (HOMO). In I it is seen that the splitting between the lowest empty MO (LEMO) and the HOMO of the dione system is generally increased by the perturbation of the B_2 bonding MO's of the diene π system. The result of including all of the intervening σ orbitals is depicted in II with the net effect being a reduced splitting. The orbitals which do not interact strongly with the orbitals of interest have been omitted from Figure 2 for clarity.

The interaction of nonconjugated π electrons has been of considerable theoretical and experimental interest.[9] Hoffmann and coworkers have recently distinguished between (1) direct through-space overlap and (2) through-bond or hyperconjugative mechanisms for interactions of π-electron systems.[10–12] In particular they have demonstrated that the through-bond mechanism can be considerable for nonplanar systems and can significantly alter the relatively large splitting of interacting degenerate π systems within a molecule. For example, the splitting due to interactions of the double bonds of 1,5-cyclooctadiene in the boat conformation as calculated for through-space interaction is reduced by 71% when the 2-3 and 6-7 bonds are included.[10]

The diketones studied in this work present two interesting aspects which are not encountered in systems where equivalent MO's interact to yield relatively large splittings and the transition electrons are initially in bonding MO's. First, the interaction of the nonequivalent dione and diene MO's leads to relatively smaller splittings. The second aspect is that the electron undergoing transition is initially in a nonbonding

(9) Footnote 1 of ref 10 provides a thorough bibliography.

(10) R. Hoffmann, E. Heilbronner, and R. Gleiter, J. Amer. Chem. Soc., 92, 706 (1970).

(11) R. Hoffmann, A. Imamura, and W. J. Hehre, ibid., 90, 1499 (1968).

(12) R. Hoffmann, Accounts Chem. Res., 4, 1 (1971).

orbital. It is evident in Figure 2 that this orbital is significantly elevated when interacted with the diene system including the σ bonds. As a result, the splitting (reflected by the n $\rightarrow$ π^* transition) is small enough for the through-space interaction that the through-bond interaction predominates. To our knowledge, this is the only example of a situation in which the through-bond correction actually predominates and exhibits its effect so clearly in the electronic spectra of a molecule.

(13) National Aeronautics and Space Administration Predoctoral Trainee, Sept 1, 1967–Aug 31, 1969.
(14) Supported by Development Award No. 1-K4-GM-42572 from the National Institutes of Health.

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Bending Nitrosyls in Tetragonal Complexes

Sir:

Nitric oxide coordinates to transition metal ions in either a linear or bent manner.[1] From a structural viewpoint, the linear arrangement has been viewed in terms of NO^+ and the bent arrangement in terms of NO^-, but it seems clear that these bonding descriptions represent too rigid and simplistic a view. As yet, the factors which result in one bonding mode over the other in different nitrosyl complexes have not been fully delineated, although discussions regarding individual systems have appeared.[2] We have undertaken an examination of nitrosyl bonding in five- and six-coordinate tetragonal complexes, and present herein a correlation of the two bonding modes which allows one to predict which of the arrangements is preferred in a given tetragonal complex.

The procedures employed in this study are similar to those used by Walsh for triatomic systems such as NO_2 and NO_2^+.[3] The two geometries of interest in the five-coordinate *tetragonal* case are both square-based pyramids, the first possessing a linearly coordinated axial nitrosyl and the second having a bent axial nitrosyl. On the left side of Figure 1, an approximate energy level ordering for the linear nitrosyl complex of C_{4v} symmetry is presented, while on the right side of the figure the energy levels for the bent nitrosyl complex of C_s symmetry are drawn. In correlating the molecular energy levels and orbitals in the two limiting structures, we join only those levels transforming under the same irreducible representation in C_s sym-

(1) For a recent review of nitrosyl complexes, see B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966).
(2) Some representative examples include the following papers: (a) P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, 87, 3340 (1965); (b) D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.*, 410 (1965); (c) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, 5, 823 (1966); (d) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 90, 4486 (1968); D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 7, 2345 (1968); (e) D. J. Hodgson and J. A. Ibers, *ibid.*, 8, 1282 (1969); (f) D. A. Snyder and D. L. Weaver, *ibid.*, 9, 2760 (1970); (g) G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970); (h) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 9, 1105 (1970); (i) D. M. P. Mingos and J. A. Ibers, *ibid.*, 10, 1035 (1971); (j) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, 10, 1043 (1971); (k) D. M. P. Mingos and J. A. Ibers, *ibid.*, 10, 1479 (1971).
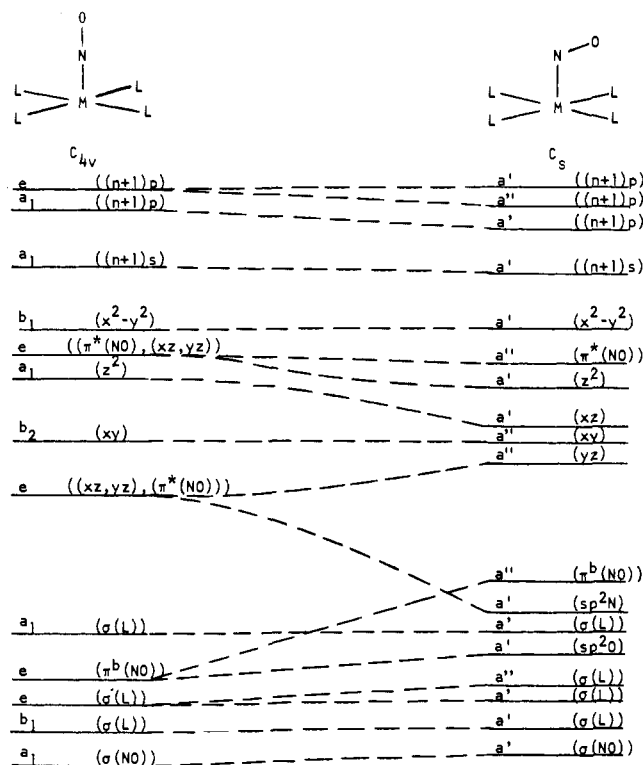(3) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

Figure 1. An orbital correlation diagram for the bending of nitrosyls in five-coordinate tetragonal systems. The orientation of the bent nitrosyl group in C_s symmetry is toward one of the basal ligands as has been observed in all of the five-coordinate tetragonal systems with bent nitrosyls studied to date.

metry, and we adhere to the noncrossing rule. Several important correlations are thus found to arise. First, the low-energy doubly degenerate $\pi^b(NO)$ set in C_{4v} symmetry splits as the M–N–O bond angle is changed from 180°, with one member of the set remaining as a $\pi^b(NO)$ function while the other member becomes an oxygen-based nonbonding orbital of a' symmetry. Second, the π-bonding e level delocalized over the metal d_{xz}, d_{yz} orbitals and the nitrosyl $\pi^*(NO)$ functions splits in the reduced symmetry and correlates with the metal d_{yz} (a'') level and the nonbonding orbital of a' symmetry localized on the nitrosyl nitrogen atom. This latter correlation is of fundamental significance, since it is precisely the change in orbital character from a primarily metal-based π function to one localized on the nitrosyl group which explains the oxidative-addition process in the coordination of NO^+ to certain d^8 metal ions.[4] A third correlation is that of the d_{z^2} level in C_{4v} symmetry, which is σ^* with respect to the metal–nitrosyl bond, correlating with the largely nonbonding d_{xz} (a') level in C_s symmetry. Lastly, the higher energy π^* e level splits and correlates with the a'' $\pi^*(NO)$ level and the metal-based a' level denoted as d_{z^2}.

The correlation diagram thus implies that for a 20-electron system composed of 10 electrons in the ligand σ^b functions, 4 electrons in the $\pi^b(NO)$ set, and a d^6 metal ion, the C_{4v} configuration in which strong M→ NO π bonding exists is the geometry of the ground

(4) In this regard, we note that the delocalized π-bonding e level in C_{4v} symmetry is traditionally assigned to the metal d_{xz}, d_{yz} set, thus leading to the NO^+ formulation for the nitrosyl, regardless of the per cent of metal character calculated for the molecular orbitals belonging to this level.