Tetrahedron. Vol. 25, pp 5451 to 5464. Pergamon Press 1969. Printed in Great Britain

THE ELECTRONIC STRUCTURE OF RESONANCE STABILIZED DICYANOCARBENE AND CARBONYLCARBENE*

J. F. OLSEN
Department of Chemistry, Staten Island Community College, Staten Island, New York, New York 10301
and
L. BURNELLE
Department of Chemistry, New York University, Washington Square, New York, N.Y. 10003

(*Received in USA* 27 *May* 1969; *Received in the UK for publication* 22 *July* 1969)

Abstract—Molecular wavefunctions for C_2O and C_3N_2 have been computed by the extended Hückel and by the INDO methods. Both procedures lead to a linear triplet ground state for the two molecules. In C_2O there is a charge shift in the σ-framework toward oxygen but the opposite effect takes place in the π-orbitals, with the result that the total charges are primarily located on the carbons (negative on the terminal atom, positive on the middle atom). The reactivity of the compound with olefins is then analyzed; INDO calculations on the biradical intermediate resulting from the reaction of ethylene with C_2O indicate a charge transfer of 0·11e to C_2O, essentially due to the polar effect of oxygen. These results point to an electrophilic character for the compound, in agreement with the observations of Bayes *et al.*[6]

The π-bond order for the CC bond in C_3N_2 is found to be remarkably small (1·05), which explains the low resistance to bending around the central atom. The zero-field splitting parameters derived from the spin densities are in good agreement with the values obtained from the ESR spectrum.

INTRODUCTION

IN A continuation of our work on molecules related to C_3, we wish to present herein the results of some relatively simple quantum chemical calculations on the molecules C_3N_2 and C_2O. The first paper in this series concerned itself with the electronic structure of carbon suboxide.[1]

Carbon suboxide undergoes a photochemical reaction with olefins, the net effect of the reaction being an insertion of a single C atom yielding a mixture of allenes and alkynes along with two molecules of CO[2]. When C_3O_2 labeled in the central position is used in the photolysis reaction, the resulting allene is found to have the labeled carbon primarily in the central position.[3] The reactive intermediate in the photolysis of C_3O_2 is thought to be the C_2O molecule.[2] C_2O acts then essentially as a C atom donor in its reactions with olefins.[2]

Baker *et al.*[4] studied the relative reactivities of a series of olefins in the photolysis of C_3O_2. These workers found that the olefin reactivity decreased with increasing substitution at the double bond and concluded that the reactive intermediate in the photolysis of C_3O_2 possessed nucleophilic properties. In complete contrast, Bayes *et al.*[5,6] performed similar reactivity studies and found that the reactivity of the olefin increased with increasing substitution. These workers attributed electrophilic properties to the reactive intermediate.

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* Work supported by the U.S. Army Research Office (Durham).

Bayes *et al.*[5,6] have also demonstrated that the properties of the reactive intermediate generated in the photolysis of C_3O_2 are strongly dependent on the wavelength of the photolyzing light used. Thus they have found that when light of 2900A or greater wavelength is used, the intermediate produced has electrophilic properties. This intermediate is thought to be the C_2O molecule in a $^3\Sigma^-$ electronic state. If 2500A light is used, the reactive intermediate is found to be indiscriminate in its reactions with olefins. In this case the intermediate is thought to be the C_2O molecule in a $^1\Delta$ electronic state.

To our knowledge C_2O has not yet been the object of a detailed quantum-mechanical study.[2] In this paper we have used two simple quantum-mechanical methods, with a view to shedding some light on the physical and chemical properties of the compound.

Dicyanocarbene, C_3N_2, undergoes reactions that are characteristic of carbene species.[7] This molecule is also moderately selective in its CH insertion reactions, indicating a stabilized carbene. In addition, C_3N_2 has also been found to bend very easily about the central C atom; the bending frequency is predicted to be very small ($\sim$20 cm^{-1}).[8] Although the bending frequency has not been measured directly for C_3N_2, in C_3[9] and C_3O_2[10] it has been measured at 63 cm^{-1}, which is indeed very low.

In our previous paper,[1] we have discussed this feature in terms of the electron density distribution in C_3 and C_3O_2. We have thought it of interest to examine whether our interpretation would also hold in C_3N_2. The ESR spectrum of the compound has been analyzed recently and the zero-field splitting parameters have been determined.[11] The computation of these parameters has provided a test for the adequacy of our wave functions.

Computational methods

In this study we have employed the extended Hückel MO (XHMO) method[12] as used extensively by Hoffmann[13] and an approximate Hartree–Fock-SCF model[14] developed by Pople *et al.*[15] The MO's are approximated as linear combinations of atomic orbitals (LCAO) in both methods. The basis set of atomic orbitals used in these calculations were 2s and 2p Slater type atomic orbitals.[16] The details of the XHMO method used in this study have been described previously.[1]

Two versions of the approximate SCF method developed by Pople *et al.*[15] are enjoying remarkable success. On one level of approximation is the complete neglect of differential overlap (CNDO) method.[17] The CNDO method is characterized by completely neglecting atomic overlap distributions of the type $\phi_\mu(1)\phi_\nu(1)$ $(\nu \neq \mu)$, in electron interaction integrals. On a higher level of approximation is the intermediate neglect of differential overlap (INDO)[18] method. In this method, the product of two different atomic orbitals $\phi_\mu(1)\phi_\nu(1)$ associated with electron (1) are retained only in one-center electron interaction integrals.

The molecules C_2O and C_3N_2 presumably have triplet ground states with two unpaired electrons. The approximations made in the CNDO method are too extreme to give a proper account of the spin polarization contributions to the unpaired electron distribution. The INDO method, on the other hand, is capable of yielding molecular wavefunctions that accommodate exchange polarization.[18] We have therefore used the INDO method in this study.

This method uses a spin-unrestricted orbital wavefunction allowing different spatial MO's for electrons with different spins.[19] Thus, the double occupancy criterion of the MO's is relaxed and this leads to negative as well as positive spin densities. An unrestricted INDO–LCAO–SCF molecular wavefunction for m α electrons and n β electrons ($m \geqslant n$) has the form:

$$\psi = |\psi_1^\alpha(1)\alpha(1)\ldots\psi_m^\alpha(m)\alpha(m)\psi_1^\beta(m+1)\beta(m+1)\ldots\psi_n^\beta(n)\beta(n)| \qquad (1)$$

where ψ_i^α and ψ_i^β form two different orthonormal sets

$$\psi_i^\alpha \quad \sum_\mu C_{\mu i}^\alpha \phi_\mu; \qquad \psi_i^\beta = \sum_\mu C_{\mu i}^\beta \phi_\mu. \qquad (2)$$

The $C_{\mu i}^\alpha$ and the $C_{\mu i}^\beta$ in (2) are the LCAO coefficients in the molecular orbitals ψ_i^α and ψ_i^β, respectively. These LCAO coefficients are determined by solving two separate F matrices in a standard SCF manner.[18] The approximations introduced in the evaluation of the atomic and molecular integrals are described in detail by Pople *et al.*[18]

The LCAO coefficients are used to construct charge-bond order matrices for α and β spin electrons, respectively, defined by:

$$P_{\mu\nu}^\alpha = \sum_i^m C_{\mu i}^\alpha C_{\nu i}^\alpha \qquad (3)$$

$$P_{\mu\nu}^\beta = \sum_i^n C_{\mu i}^\beta C_{\nu i}^\beta \qquad (4)$$

The total charge-bond order matrix for the molecule is obtained by summing the individual α and β charge-bond order matrices,

$$P_{\mu\nu} = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta \qquad (5)$$

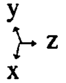
while the spin density matrix is formed by taking the difference of these same two quantities,

$$P_{\mu\nu} = P_{\mu\nu}^\alpha - P_{\mu\nu}^\beta \qquad (6)$$

It should be noted[20] that the wavefunction described by Eq. 1 is an eigenfunction of S_z but not of S^2. Thus in our case the INDO wavefunction is not a pure triplet but contains contaminants of higher spin multiplicities. A projection operator technique must be employed to obtain a pure triplet wavefunction.[21] This projection has not been performed in this study as it was hoped that the proportion of higher spin multiplets present in Eq. 1 would be small.

Since the experimental geometry for C_3N_2 and C_2O is unknown, we have employed the electron diffraction geometry[22] of C_3O_2 for these molecules. This corresponds to a CC bond length of 1·28A and a CX (X = O, N) bond length of 1·16A. The labeling of axes and atoms was taken as follows:

1 2 2 2 1 3 3
C—C—O N—C—C—C—N



Carbonyl carbene (C_2O). The reactive C_2O molecule is predicted to be linear according to the Walsh[23] correlation diagrams for AB_2 and ABC type molecules. The following order of molecular orbitals for linear C_2O was produced by the XHMO method:

$$(1\sigma)^2(1\sigma')^2(2\sigma)^2(1\pi')^4(2\sigma')^2(1\pi)^2: {}^3\Sigma^-, {}^1\Delta, {}^1\Sigma^+,$$

where the prime orbitals would correspond to ungerade orbitals in linear AB_2 molecules. This ordering of MO's by the XHMO method gives rise to three states, all of which are degenerate. This is inherent to the XHMO method which does not include electron interaction, and consequently can only give the average energy of an electron configuration. Thus the calculations performed using the XHMO method cannot make an outright prediction as to the ground state of this molecule.

Upon bending, each π orbital splits into two levels; one which is relatively unaffected by the bending is formed from 2p orbitals perpendicular to the plane of the distorted molecule and belongs to the a″ representation of the C_s point group. The other one is formed from s and p orbitals located in the plane of the bent molecule and is of a′ symmetry. A plot of the XHMO one-electron energies versus bending about the apex angle for C_2O is illustrated in Fig. 1. It should be noted from Fig. 1, that the 6a′ and the 7a′ levels cross in the vicinity of 100°. This crossing should not actually take place as it violates the non-crossing rule. The one-electron energies are probably best represented schematically by the broken curves in the figure. Since in linear C_2O two electrons are located in the degenerate 1π orbital, the XHMO method will give rise, upon bending, to a splitting of the lowest computed linear state into three levels. These will have the following electronic configurations: $(2a'')^2$, $(2a'')\,(6a')$ and $(6a')^2$, respectively (all the lower orbitals up to 5a′ remain doubly occupied), We illustrate in Fig. 2 the variation of the energies of these three configurations as a function of the apex angle. The $(2a'')^2$ configuration has its minimum energy for a CCO angle

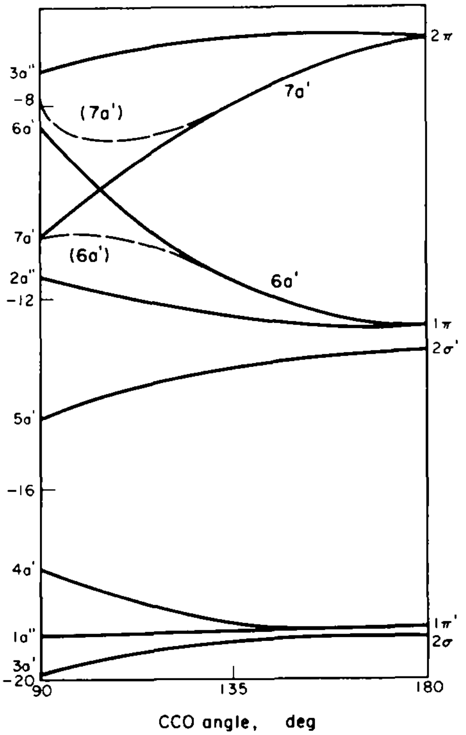


FIG. 1 XHMO orbital energies versus angle for C_2O.

equal to 145°. The minimum lies 0·29 eV below the energy of the (2a″) (6a′) configuration at the same angle, and 0·20 eV below the energy of the linear system. The smallness of these differences is a consequence of the small splitting (for a CCO angle in the vicinity of 145° at least) exhibited by the 1π orbital when the molecule bends.

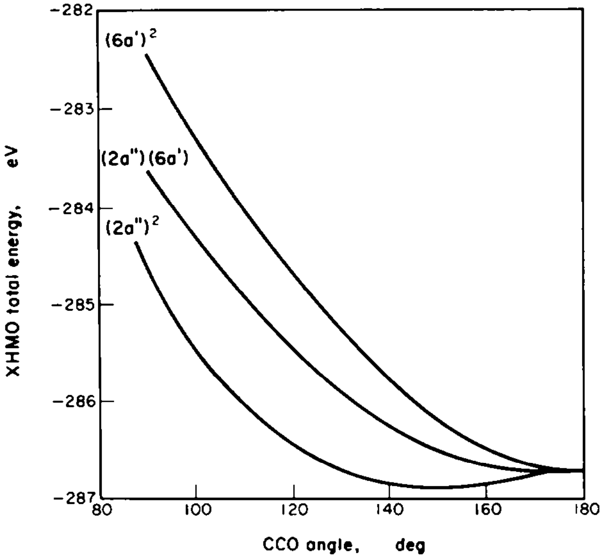


FIG. 2 Energies of the lower XHMO configurations of C_2O as a function of the apex angle.

Under such conditions it may very well happen that in actuality, the lowest electronic state does not correspond to the double occupancy of the lowest orbital, but to the triplet associated with a single occupancy of each orbital. This is actually the case in methylene,[24] where the behavior of the orbital energies is comparable in several respects to the one observed in C_2O, and where it is known that the interelectronic interaction actually causes the lowest state to be a triplet. Methylene is also characterized by a small splitting of the components of the π orbitals. Hoffmann[24] labels them σ and p, respectively, the former lying in the plane of the bent molecule, the latter being perpendicular to that plane. When the molecule bends, the σ orbital lies below the p orbital, contrary to what we observe in C_2O for the 1π MO. In a study on substituted methylenes, Hoffmann[24] proposes the following criterion for determining which configuration has the lowest energy: if, at the angle at which the σ^2 configuration is minimized, the splitting between the two components σ and p is smaller than 1·5 eV, the ground state will probably be the triplet derived from the σp configuration. If we apply the same criterion to C_2O, we are led to predict that the ground state of this molecule is the triplet correlating with the (2a″)(6a′) configuration, i.e. it is the linear triplet $^3\Sigma^-$. Experimental evidence is in favor of a linear geometry for this triplet molecule.[25] In addition, the first excited singlet state is predicted by the XHMO method to be a bent $^1A'$ state which correlates with $^1\Delta$.

The INDO method, which explicitly includes electron interaction, also predicts the ground state of the molecule to be the linear triplet. The calculated INDO potential curve for the triplet state of C_2O is fairly similar to the (2a″)(6a′) curve illustrated in Fig. 2. The triplet state is predicted to be 1·04 eV more stable than the singlet state in the linear form of this molecule. The determinantal wavefunction for the linear singlet is not an eigenfunction of the orbital angular-momentum operator and is really a mixture of the $^1\Delta$ and $^1\Sigma^+$ states. Configuration interaction (CI) would have to be employed in order to separate these states. Assuming that the separation between the $^1\Delta$ and the $^1\Sigma^+$ states is similar to that found in molecular oxygen (0·65 eV),[26] one comes to the conclusion that the splitting produced by CI would not be large enough to bring the $^1\Delta$ or $^1\Sigma^+$ state below the $^3\Sigma^-$ state. There is thus no doubt that the ground state of C_2O will be a linear triplet. The ground state INDO molecular wavefunction for this molecule is given as

$$\Psi = |\{1\sigma 1\sigma' 1\pi'_x 1\pi'_y 2\sigma 2\sigma' 1\pi_x 1\pi_y\}^{\alpha}\{1\sigma 1\sigma' 2\sigma 1\pi'_x 1\pi'_y 2\sigma'\}^{\beta}| : {}^3\Sigma^-,$$

with the two extra α electrons in the degenerate pair of 1π orbitals.

The atomic charges, broken down into the σ and π components, are recorded in Table 1. These σ and π charges were obtained by assuming an *sp* hybridized σ framework for the molecule before electron redistribution occurs by the computational model. This localized model for C_2O would then have three σ electrons and one π electron on C1, two σ and two π electrons on C2, and three σ and three π electrons on oxygen. We will only discuss the INDO electron populations since they are probably more realistic than the XHMO populations[1]. The charge distributions as recorded in Table 1 reveal that the carbons are electron deficient in the σ-framework due to the electron withdrawing inductive effect of the O atom. In the π-framework, on the other hand, C1 is seen to become fairly electron rich due in part to the "back-bonding" of the oxygen $n\pi$ electrons. This leads to total charges that are primarily located on the C atoms in the ground state of this triplet molecule.

In addition to the distribution of the paired electrons in this molecule, the distribution of the unpaired electrons should prove informative especially in regards to reactivity. The distribution of the unpaired electrons, as revealed by the spin densities, are recorded in Table 2. We have also performed INDO calculations on singlet and triplet NCN (R_{CN} = 1·30A) at various apex angles. Cyanonitrene, NCN, which is isoelectronic with C_2O, is predicted by the INDO method to have a $^3\Sigma_g^-$ ground state, in agreement with experiment.[27a] The unpaired electron distributions for linear NCN are also recorded in Table 2. The unpaired electron distributions in linear NCN and linear C_2O indicate that the terminal atoms in these molecules contain the excess positive spin density. Those orbitals which are associated with the β spin electrons are polarized towards the central carbon atom resulting in a net negative spin density at this atom. The large difference in the negative spin densities, observed for these molecules at the central C atom, is due mainly to the form of the highest occupied MO (homo). One component of the degenerate π-homo for these molecules is recorded in Table 3. The C_2O homo is seen to have a coefficient on the central C atom which leads to a positive contribution to the spin density at this atom. The NCN homo, on the other hand, is seen to be of π_g symmetry which leads to no net contribution to the central atom spin density from this orbital. This gives rise to the large negative spin density on carbon in linear NCN. The unpaired electrons in triplet C_2O and NCN are seen to be delocalized over the three atoms (as revealed by the spin densities of Table 2). Consequently, these molecules would be expected to show some discrimination in their reactivities compared to triplet methylene which has its unpaired electrons localized on the central C atom. This selectivity is found experimentally for C_2O[6] and NCN.[27b]

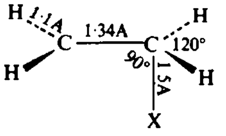
The atomic charges in linear triplet C_2O speak for a carbene possessing nucleophilic properties since Cl, which is the reactive site in this molecule (*vide infra*), has a fairly large negative charge. Consequently, basing reactivities solely on the ground state charge distributions would tend to favor the reactivity pattern found by Baker *et al.*[4] However, a more detailed analysis of the question should be based on the features of the transition state of the reaction. We are going to see that such a study reveals that other factors, such as, for example, the polar effect exerted by the O atom of C_2O in the course of the reaction, play a non-negligible role in determining the reactivity of the compound. We will see that one is then led to label C_2O as an electrophilic reagent, in agreement with the experimental observations of Bayes *et al.*[6]

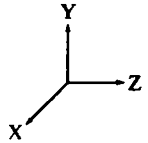
We record in Table 4 the relative reactivities of triplet O atoms, triplet C_2O molecules, and triplet CH_2 molecules with various olefins, as tabulated by Bayes *et al.*[6] Whereas triplet CH_2 appears to be fairly unselective, triplet O atoms and triplet C_2O molecules exhibit electrophilic properties, according to these data. The values collected in Table 4, together with the activation energy differences found for the O atom olefin reactions and the C_2O molecule olefin reactions,[6, 28] are in agreement with a relatively loose O atom—olefin transition state with some charge-transfer characteristics.[28] The C_2O olefin transition state is probably relatively tighter with more biradical character than the corresponding O atom-olefin transition state. The biradical nature of the C_2O-olefin transition state is revealed by the reactivity of C_2O with butadiene. Diphenylcarbene[29] and propargylene[30] (isoelectronic with C_2O), both molecules of which are known to have triplet ground states, react remarkably fast with butadiene. Indeed, Skell *et al.*[29, 30] have found that both of these compounds are selectively consumed (over 100 times more rapidly than with isobutylene) by butadiene compared to simple olefins. We are inclined to believe that the C_2O-olefin transition state lies between the olefin-O atom transition state and the olefin-propargylene transition state, probably closer to the former.

If one was to consider only the spin densities as the criterion of reactivity of C_2O, then one would be forced to predict nearly equal reactivities at the two terminal atoms in this molecule. However, there is no experimental evidence[2–6] which indicates any tendency for C_2O to react at the oxygen terminus. We feel that the form of the highest occupied MO is here the predominant factor. It is seen from Table 3 that the major contributor to this MO is the p (p_x or p_y) atomic orbital coefficient at the carbon terminus. Consequently, this terminus should present the greatest overlap possibilities with a reacting olefin molecule at the transition state. On the other hand, the overlap at the oxygen terminus should be much smaller.

This qualitative reasoning could, not too easily, be verified by exploring the calculated energies of the various olefin-C_2O adducts. However, this would involve an enormous amount of calculations. Instead of performing all these calculations, we have taken the theoretical license of calculating, rather arbitrarily, the biradical intermediates resulting from the reaction of ethylene with C_2O (both termini) and with a triplet O atom. Only the INDO method has been used in these computations. The biradical model may not be a good representation of the transition state for these processes, expecially in the olefin-O atom case. However, the charge distributions should be similar in the biradicals since both triplet O atoms and triplet C_2O are assumed to possess electrophilic properties.

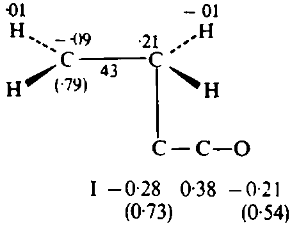
The following configurations and geometries were assumed for the biradical intermediates:

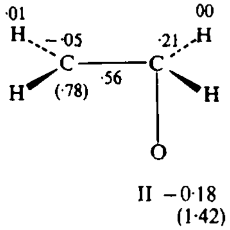




where X = a triplet O atom, or a triplet C_2O molecule oriented parallel to the z axis, and presenting to the olefin either its carbon or its oxygen terminus. The bond lengths of C_2O were kept the same as used for the ground state. In agreement with our qualitative reasoning, the biradical intermediate resulting from the C_2O oxygen terminus attack was found to be 6·8 eV less stable than the corresponding biradical resulting from the Cl terminus attack. Although the magnitude of this energy difference between the two biradical intermediates is perhaps largely exaggerated, it is very suggestive that the Cl attack should be highly favored over the O atom attack.

The electron distributions found in the biradical intermediates produced from ethylene and C_2O and ethylene and O atoms are as follows:

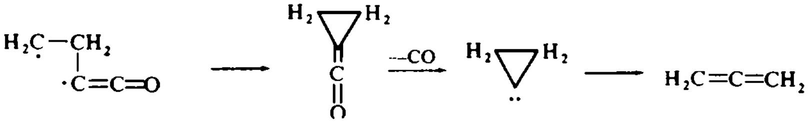




where the signed numbers refer to atomic charges, the parenthetic numbers represent the *atomic* spin densities, and the number between the CC bond of ethylene represents the INDO π-bond order. As might have been expected, both biradicals are seen to have fairly similar electron distributions. Both the C_2O and O atom biradical intermediates are seen to possess some charge-transfer characteristics. In the O atom biradical this amounts to 0·18 electrons transferred to the O atom, while in the case of C_2O this charge transfer amounts to a total of 0·11 electrons. This charge transfer in the C_2O biradical is mainly due to the presence of the O atom which has increased in charge density significantly compared to the ground state charge density of this atom. The "free" C atom of ethylene is seen to be slightly electron rich in the biradical intermediates. However, it is electron deficient in the σ framework and in addition, the transition states in these olefin addition reactions probably occurs before the C_2O molecule or the O atom is localized on one of the olefinic C atoms. Consequently, both C atoms will in all probability be positively charged at the transition state. A calculation in which the C_2O molecule is located 1·5 A below the ethylene molecule and symmetrically placed (between the CC bond) in the YZ plane, along the Y axis, indicates that a fair amount of positive charge (0·13 electron units) has developed in the σ framework of the olefin*. This development of positive charge on the olefinic carbons should be stabilized by electron donating alkyl groups. This is in line with the electrophilic reactivity sequence observed by Bayes *et al.*[6]

* Although the total change is not as large it is still positive (0·04 electron units).

The positive spin densities in the biradical I are also interesting. There is seen to be an increase in the amount of positive spin density at C1 in the biradical intermediate compared to the spin density at this center in the isolated molecule. The unpaired electron distribution in the 2s orbital has also increased considerably (~7 fold) in the biradical intermediate. These unpaired electron distributions are consistent with the proposed cyclization of the biradical intermediate to the cyclopropylidene ketene, which loses a molecule of CO to form cyclopropylidene; the latter is known to rearrange to allene:



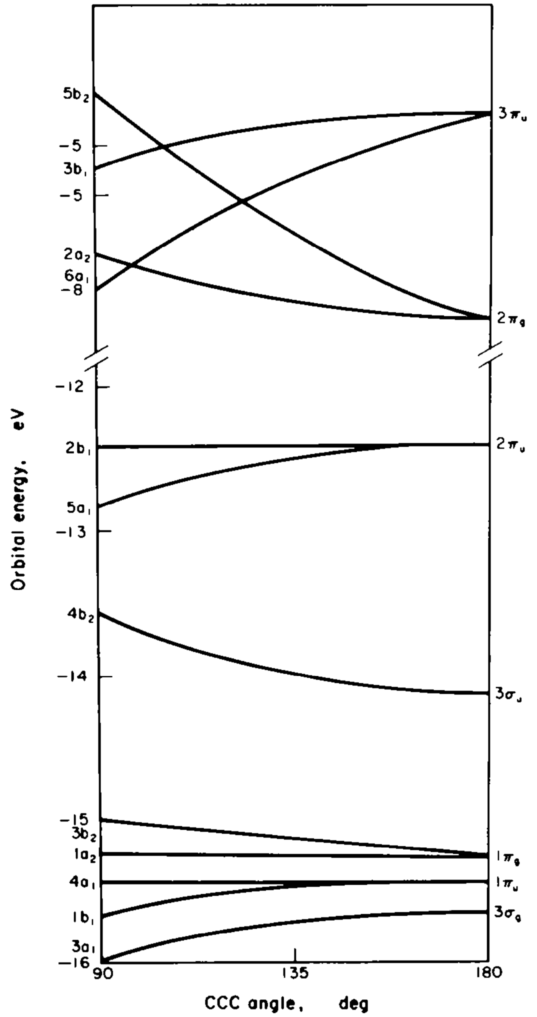


FIG. 3 XHMO orbital energies versus apex angle for C_3N_2.

Dicyanocarbene (C_3N_2). The XHMO method predicts C_3N_2 to be most stable in the linear form. The corresponding XHMO electronic configuration is:

$$1\sigma_u^2\, 1\sigma_g^2\, 2\sigma_g^2\, 2\sigma_u^2\, 3\sigma_g^2\, 1\pi_u^4\, 1\pi_g^4\, 3\sigma_u^2\, 2\pi_u^2:\quad {}^3\Sigma_g^-,\ {}^1\Delta_g,\ {}^1\Sigma_g^+$$

This electron configuration gives rise to three states, all which are degenerate in XHMO theory. Following the procedure used for C_2O, we record in Fig. 3 the orbital energy diagram for C_3N_2 as computed by the XHMO method. The lower energy configurations of bent C_3N_2 are $(5a_1)$,^{2} $(5a_1)$ $(2b_1)$, and $(2b_1)$,^{2} respectively. Their energy variation with the bond angle is illustrated in Fig. 4. The results indicate that all three configurations are stable with respect to in-plane bending. The curves also suggest that C_3N_2 should have a linear triplet ground state. A similar conclusion was reached by Hoffmann *et al.*[24] for this molecule. Subjecting the energies of the $(5a_1)$ $(2b_1)$ configuration to a polynomial fit leads to a calculated bending force constant of 0·12 mdyn/A, which should be compared with the value of 0·03 mdyn/A estimated by Smith and Leroi.[8] The form of the highest occupied MO (Table 3) for the molecule also suggests that there should be a fairly low resistance to bending.

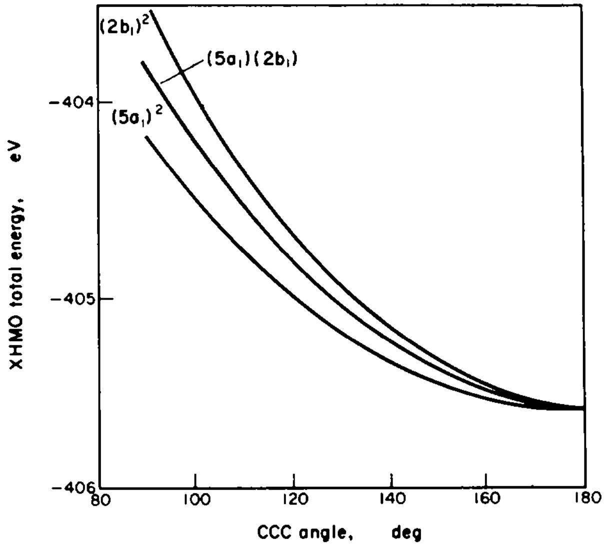


FIG. 4 Energies of the lower XHMO configurations of C_3N_2 as a function of the apex angle.

The INDO method also predicts the ground state of C_3N_2 to be a linear triplet. That the molecule is a linear triplet has also been demonstrated experimentally.[11] The INDO ground state wavefunction is as follows:

$$\Psi = |\{1\sigma_g\, 1\sigma_u\, 2\sigma_g\, 2\sigma_u\, (1\pi_u)^2\, (1\pi_g)^2\, 3\sigma_g\, 3\sigma_u\, (2\pi_u)^2\}^\alpha$$
$$\mathrm{X}\{1\sigma_g\, 1\sigma_u\, 2\sigma_g\, 2\sigma_u\, (1\pi_u)^2\ (1\pi_g)^2\, 3\sigma_g\, 3\sigma_u\}^\beta|:\ {}^3\Sigma_g^-,$$

where $(1\pi_u)$,^{2} for example, indicates a single occupancy of the x and y components of the $1\pi_u$ orbital. This state is 1·31 eV more stable than the singlet mixture of $^1\Delta_g$ and $^1\Sigma_g^+$ states.

The electron populations recorded in the tables, together with an INDO central CC π-bond order of 1·05 (this number represents the sum of the p_x and the p_y INDO bond orders) and an INDO CN π-bond order of 1·61, are consistent with the following resonance structures contributing to the ground state of this triplet molecule:

$$\mathrm{N{\equiv}C{-}\underset{\bullet}{\dot{C}}{-}C{\equiv}N} \quad \mathrm{N{\equiv}C{-}\dot{C}{=}C{=}\dot{N}} \quad \mathrm{\dot{N}{=}C{=}\dot{C}{-}C{\equiv}N} \quad \mathrm{\dot{N}{=}C{=}C{=}C{=}\dot{N}}$$

Those resonance structures which act to reduce the π bond population between the central CC bonds serves to lower the bending force constant in this molecule. This situation is very similar to the one we have observed in carbon suboxide,[1] where the central CC π-bond order was computed to be 1·24 and a CO π-bond order 1·39.

The INDO spin densities of C_3N_2 reveal that the terminal nitrogen atoms and the central carbon atom carry the positive spin densities, while the carbons of the nitrile groups are seen to have a large net negative spin density. Wasserman *et al.*[11] observed the ESR spectrum of this molecule (generated photolytically from $(NC)_2\,C{=}N_2$) and obtained the following zero-field splitting parameters:

$$D = 1{\cdot}002\ \mathrm{cm}^{-1} \text{ and } E < 0{\cdot}002\ \mathrm{cm}^{-1}$$

A non-zero E value indicates the deviation of the triplet molecule from cylindrical symmetry, while the D value measures the extent to which the spin degeneracy of the triplet state is removed by dipole-dipole interactions of the unpaired electrons.[31] D is roughly proportional to the average of the inverse cube of the distance between the two electrons, $\langle 1/r_{ij}^3 \rangle$. The above measured zero-field splitting parameters are considered to be consistent with a linear structure for this molecule.[11]

Wasserman *et al.*[11] have used the following expression for the evaluation of D,

$$D = \sum_i \rho_i{}^2 D_i \tag{7}$$

where ρ_i is the spin density in one orbital of the degenerate π set of the *ith* atom and D_i is an empirical parameter having the value 1·86 cm^{-1} (spectroscopic value)[32a] when $i = N$ and 0·74 cm^{-1} when $i = C$.[32b] Assuming the following spin densities in C_3N_2: $\rho_N = 0{\cdot}40$, $\rho_{C2} = -0{\cdot}20$, and $\rho_{C1} = 0{\cdot}60$, Wasserman *et al.*[11] using Eq. 7 have calculated a D value of 0·97 cm^{-1}. This computed D value also includes a 0·05 cm^{-1} contribution from the two-center terms that contribute to D.

Employing Eq. 7 and the INDO π-spin densities recorded in Table 2 together with the 0·05 cm^{-1} contribution from two center terms leads to a computed D value of 1·07 cm^{-1}. The computed value of D reduces to 0·99 cm^{-1} when a CC bond length of 1·35 A (minimum energy bond length by INDO) is employed. Wasserman *et al.*[11] also obtained a D value of 1·54 cm^{-1} for cyanonitrene. The corresponding INDO spin densities for this molecule recorded in Table 2 leads to a calculated D value of 1·82 cm^{-1}. Clearly, as has been pointed out by Wasserman *et al.*,[11] large negative spin densities are necessary in these molecules in order to avoid a much lower calculated D value. The INDO unrestricted wavefunctions are apparently fairly good for these molecules. This is of course only true if the validity of Eq. 7 is accepted.

The extensive delocalization of the unpaired electrons in this molecule speak for a selective carbene. This selectivity has been observed by Ciganek[7] for singlet C_3N_2. The form of the highest occupied molecular orbital which is largely localized on the central C atom indicates that C_3N_2 should react preferentially at this center. Experimentally,[7] reaction only occurs at the central carbon and not at the terminal nitrogens, at least to our knowledge.

CONCLUSIONS

The two methods used in this paper have provided a coherent picture of the electronic structure of carbonylcarbene, cyanonitrene, and dicyanocarbene, which are predicted to be resonance stabilized triplets. It is encouraging to observe that the XHMO and the INDO methods are in agreement as to the nature of the ground state of C_2O and C_3N_2. A point worthy of notice is the importance of the highest occupied MO, which appears to govern to a large extent the reactivity of the compounds studied here. In the case of C_2O, an exploratory investigation on the transition state of the addition reaction with ethylene has brought evidence in favor of an electrophilic character for the compound. Furthermore, that the INDO wave functions provide a fairly good picture of the electron distributions in these molecules is evidenced by the good agreement with the ESR results.

Table 1. INDO Charges of linear CCO, NCN, HCH and C_3N_2

			Molecule		
Atom:	Orbital	CCO	NCN*	HCH†	NCCCN
C1	σ	0·143	—	—	−0·029
	π	−0·374	—	—	0·006
	$\sigma + \pi$	−0·231	—	—	−0·023
C2	σ	0·090	0·040	−0·178	0·054
	π	0·166	0·154	0·000	0·112
	$\sigma + \pi$	0·256	0·194	- 0·178	0·166
X‡	σ	−0·233	−0·020	—	−0·039
	π	0·208	−0·076	—	−0·114
	$\sigma + \pi$	−0·025	−0·096	—	−0·153
H	σ	—	—	0·089	—

* $R_{CN} = 1·30A$
† $R_{CH} = 1·10A$
‡ X = O, or N

Table 2. INDO Orbital spin densities in linear C_2O, NCN, HCH and C_3N_2

Atom	Orbital	CCO	NCN	HCH	NCCCN
C1:	2s	0·025	—	—	0·049
	2x	0·525	—	—	0·518
	2y	0·525	—	—	0·518
	2z	−0·015	—	—	0·030
C2:	2s	−0·012	−0·057	0·128	−0·035
	2x	−0·011	−0·350	1·000	−0·211
	2y	−0·011	−0·350	1·000	−0·211
	2z	−0·024	−0·044	0·067	−0·032
X:	2s	0·022	0·029	—	0·023
	2x	0·487	0·675	—	0·452
	2y	0·487	0·675	—	0·452
	2z	0·002	0·022	—	0·004
H:	1s	—	—	−0·097	—

TABLE 3. FORM OF THE HOMO* AND THE CORRESPONDING EIGENVALUE FOR LINEAR C_2O, NCN AND C_3N_2 ACCORDING TO THE XHMO AND THE INDO METHODS

Molecule	C_2O		NCN		C_3N_2	
Method	XHMO	INDO	XHMO	INDO	XHMO	INDO
Eigenvalue (eV)	−12·45	−13·62	—	−14·85	−12·37	−11·70
Atom						
C1†	0·75	0·73	—	—	0·69	0·66
C2	0·47	0·51	—	—	0·24	0·02
C3	—	—	—	—	0·24	0·02
X2	−0·28	−0·51	—	0·71	−0·42	−0·53
X3	—	—	—	−0·71	−0·42	−0·53

* One component of the doubly degenerate set is tabulated.

† See text for the atom numbering scheme.

TABLE 4. RELATIVE REACTIVITIES OF TRIPLET OXYGEN ATOMS, TRIPLET C_2O AND TRIPLET CH_2[6]

Reactant	$O(^3P)$	$C_2O(^3\Sigma^-)$	$CH_2(^3\Sigma_g^-)$
Ethylene	1·0	1·0	1·0
Propylene	5·8	6·1	1·0
Isobutylene	25	58	2·9
Trimethylethylene	79	100	1·8
Tetramethylethylene	102	250	2·7
1,3-Butadiene	24	210	19

Acknowledgements—The authors would like to express their sincere thanks to Dr. David Beveridge for making available to them his INDO program used for these calculations. We also would like to thank the New York University AEC Computing Center for a grant of computer time.

REFERENCES

[1] J. F. Olsen and L. Burnelle, *J. Phys. Chem.* **73**, 2298 (1969).

[2] K. D. Bayes, *J. Am. Chem. Soc.* **84**, 4077 (1962); *Ibid.* **85**, 1730 (1963).

[3] R. T. Mullen and A. P. Wolf, *Ibid.* **84**, 3214 (1962).

[4] R. T. K. Baker, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.* A975 (1966).

[5] C. Willis and K. D. Bayes, *J. Am. Chem. Soc.* **88**, 3203 (1966).

[6] D. G. Williamson and K. D. Bayes, *Ibid.* **90**, 1957 (1968).

[7] E. Ciganek, *Ibid.* **88**, 1979 (1966).

[8] W. H. Smith and G. E. Leroi, *J. Chem. Phys.* **45**, 1784 (1966).

[9] L. Gausset, G. Herzberg, A. Lagerqvist and B. Rosen, *Astrophys. J.* **142**, 45 (1965).

[10] F. A. Miller, D. H. Lemmon and R. E. Witkowski, *Spectrochim. Acta* **21**, 1709 (1965); W. H. Smith and G. E. Leroi, *J. Chem . Phys.* **45**, 1778 (1966).

[11] E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.* **87**, 2075 (1965).

[12] R. S. Mulliken, *J. Chim. Phys.* **46**, 497, 675 (1949).

[13] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

[14] C. C. J. Roothaan, *Revs. Mod. Phys.* **23**, 69 (1951).

[15] J. A. Pople, D. L. Beveridge, and N. S. Ostlund, *Intern. J. Quant. Chem.* **1**, 293 (1967); and refs cited therein.
[16] J. C. Slater, *Phys. Rev.* **36**, 57 (1930).
[17] J. A. Pople and G. A. Segal, *J. Chem. Phys.* **44**, 3289 (1966); and refs cited therein.
[18] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.* **47**, 2026 (1967).
[19] J. A. Pople and R. K. Nesbet, *J. Chem. Phys.* **22**, 57 (1954).
[20] A. T. Amos and L. C. Snyder, *J. Chem. Phys.* **41**, 1773 (1964).
[21] P. O. Löwdin, *Phys. Rev.* **97**, 1509 (1955).
[22] R. L. Livingston and C. N. R. Rao, *J. Am. Chem. Soc.* **81**, 285 (1959).
[23] A. D. Walsh, *J. Chem. Soc.* 2325 (1953).
[24] R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Am. Chem. Soc.* **90**, 1485 (1968).
[25] M. E. Jacox, D. E. Milligan, N. G. Moll and W. E. Thompson, *J. Chem. Phys.* **43**, 3734 (1965).
[26] G. Herzberg, *Molecular Spectra and Molecular Structure of Diatomic Molecules*, p. 560. D. Van Nostrand, Princeton, N.J. (1950).
[27] [a] G. Herzberg and D. N. Travis, *Can. J. Phys.* **42**, 1658 (1964).
[b] A. G. Anastassiou and H. E. Simmons, *J. Am. Chem. Soc.* **89**, 3177 (1967).
[28] R. J. Cvetanovic, *Advan. Photochem.* **1**, 115 (1963).
[29] R. M. Etter, H. S. Skrovronek and P. S. Skell, *J. Am. Chem. Soc.* **81**, 1008 (1959).
[30] R. Bernheim, R. J. Kempf, J. V. Grammas, P. S. Skell, *J. Chem. Phys.* **43**, 196 (1965).
[31] A. Carrington and A. McLachlan, *Introduction to Magnetic Resonance*, pp, 115–129. Harper and Row, New York (1967).
[32] [a] R. N. Dixon, *Can. J. Phys.* **37**, 1171 (1959);
[b] Extrapolated value from linear F_3CCH by E. Wasserman.
[33] E. Wasserman, *J. Am. Chem. Soc.* **87**, 3739 (1965).