interrelates the absolute configurations of $(-)_{589}$-*cis*-$[Co(en)_2(OH_2)_2]^{3+}$ and $(-)_{589}$-$[Co(en)_2acac]^{2+}$ in agreement with assignments previously made on the basis of circular dichroism spectra;[31] *i.e.*, the absolute configuration is Δ.

The reactant isomerization rates not only provide data essential to the determination of the rate constant for formation of $[Co(en)_2acac]^{2+}$ but also, given an assumption of mechanism, enable some estimate to be made of reactant oxygen exchange rates. Thus, if rearrangement or substitution at Co(III) is to proceed *via* dissociation of one ligand (in the case of $Co(en)_2XY^{n+}$, dissociation of X or Y would be preferred), the oxygen exchange rates of $[Co(en)_2(OH_2)OH]^{2+}$ species must exceed the rates of isomerization and inversion. The measured rates of isomerization for *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ may therefore be regarded as lower limits to their rates of exchange and for the cis ion the lower limit may be significantly increased to the rate of its loss of optical activity. Kruse and Taube[5] have shown that for the diaqua and dihydroxo complexes the rates of exchange do not greatly exceed the rates of isomerization, and their limited data indicate that this is also probably true of the hydroxoaqua complexes. The rate of formation of $[Co(en)_2acac]^{2+}$ would then exceed the rate of oxygen exchange in *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ by an order of magnitude. From the tracer experiment it appears that such is the case.

(31) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

Frontier Molecular Orbitals of 1,3 Dipoles and Dipolarophiles

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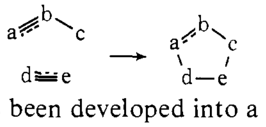
Abstract: Molecular orbital calculations have been performed by CNDO/2 and EH methods for parent and some substituted nitrilium betaines, diazonium betaines, azomethinium betaines, and carbonyl betaines and for a series of substituted alkenes. Experimental values for ionization potentials and electron affinities, calculations performed here, and calculations in the literature have been used to generate a set of frontier orbital energies and coefficients for 1,3 dipoles and dipolarophiles. The effects of substituents on orbital energies and coefficients are deduced. These frontier orbitals are of general utility in the rationalization and prediction of relative rates and regioselectivity of 1,3-dipolar cycloadditions, as well as other cycloadditions and "frontier-controlled" organic reactions.

Although fragmentary reports of the reactions of ozone, azides, and diazoalkanes with alkenes appeared prior to the 1960's,[4] the monumental work of Huisgen and coworkers led to the general concept of 1,3-dipolar cycloadditions, in which a formally zwitterionic molecule, a–b–c (the 1,3 dipole), undergoes 1,3 addition to an alkene or alkyne, d = e (the dipolarophile), to form a five-membered ring heterocycle.[5]



This reaction has been developed into a generally useful method of five-membered heterocycle synthesis, since many 1,3-dipolar species are readily available and are reactive with a wide variety of alkenes. The two all-octet resonance forms of the most common 1,3 dipoles are shown in Table I.[6]

Table I. The Common 1,3 Dipoles

Nitrilium Betaines	
$RC{\equiv}N^+C^-R_2 \leftrightarrow RC^-{=}N^+{=}CR_2$	Nitrile ylides
$RC{\equiv}N^+N^-R \leftrightarrow RC^-{=}N^+{=}NR$	Nitrile imines
$RC{\equiv}N^+O^- \leftrightarrow RC^-{=}N^+{=}O$	Nitrile oxides
Diazonium Betaines	
$N{\equiv}N^+C^-R_2 \leftrightarrow N^-{=}N^+{=}CR_2$	Diazoalkanes
$N{\equiv}N^+N^-R \leftrightarrow N^-{=}N^+{=}NR$	Azides
$N{\equiv}N^+O^- \leftrightarrow N^-{=}N^+{=}O$	Nitrous oxide
Azomethinium Betaines	
$R_2C{=}N^+(R)C^-R_2 \leftrightarrow R_2C^-N^+(R){=}CR_2$	Azomethine ylides
$R_2C{=}N^+(R)N^-R \leftrightarrow R_2C^-N^+(R){=}NR$	Azomethine imines
$R_2C{=}N^+(R)O^- \leftrightarrow R_2C^-N^+(R){=}O$	Nitrones
Oxygenated Dipoles	
$R_2C{=}O^+C^-R_2 \leftrightarrow R_2C^-O^+{=}CR_2$	Carbonyl ylides
$R_2C{=}O^+N^-R \leftrightarrow R_2C^-O^+{=}NR$	Carbonyl imines
$R_2C{=}O^+O^- \leftrightarrow R_2C^-O^+{=}O$	Carbonyl oxides
$O{=}O^+O^- \leftrightarrow O^-O^+{=}O$	Ozone

Mechanistic investigations have shown that cycloadditions of 1,3 dipoles to alkenes are stereospecifically suprafacial, solvent polarity has little effect on reaction rates, and small activation enthalpies and large negative activation entropies are generally found.[5] These facts, along with reactivity and regioselectivity phenomena, have been considered totally compatible only with a concerted four-center mechanism.[5,7] Orbital

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(3) American Chemical Society—Petroleum Research Fund Undergraduate Scholar: (a) 1971–1972; (b) 1972–1973.

(4) L. I. Smith, *Chem. Rev.*, **23**, 193 (1938).

(5) (a) R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 739; R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 565, 633 (1963); *J. Org. Chem.*, 33, 2291 (1968); (b) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972), and earlier papers in this series.

(6) For a more complete list of 1,3 dipoles and consideration of the resonance formulation of the electronic structures of these species, see ref 5a.

(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 87–89.

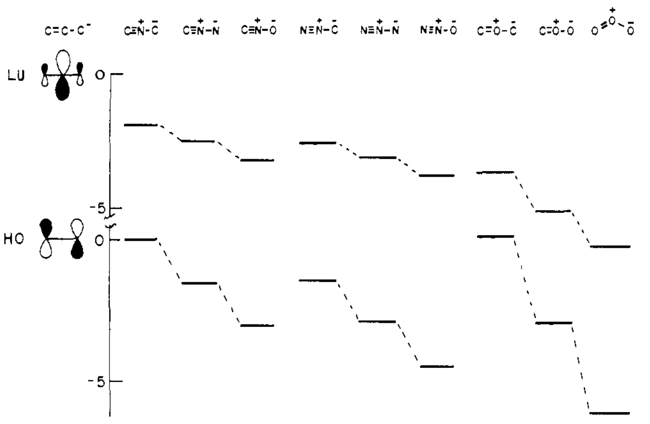

Figure 1. Qualitative π frontier orbital energies obtained from electronegativity considerations.

symmetry considerations have provided permissive, though not obligatory, theoretical evidence for the concerted mechanism,[7–9] and the observation of $[_\pi 4_s + _\pi 6_s]$ but not $[_\pi 4_s + _\pi 4_s]$ cycloadditions of 1,3 dipoles to trienes has provided further evidence for the concerted mechanism.[10]

The experimentally observed regioselectivity (selectivity in direction of addition to an unsymmetrical alkene or alkyne) of most 1,3-dipolar cycloadditions has been the most difficult phenomenon to explain. Indeed, this phenomenon (among others) has been interpreted by Firestone as evidence for a stepwise mechanism involving diradical intermediates.[11] Rationalizations of regioselectivity based on a concerted transition state model have invoked both electronic and steric effects, but regioselectivity has remained essentially an unsolved problem.[5]

Perturbation theory has been found to provide a powerful but simple method of understanding a variety of cycloadditions, and it appeared to us that perturbation theory would provide the key to the understanding of regioselectivity in 1,3-dipolar cycloadditions. This work confirms that conviction.

This paper reports a number of generalizations about the molecular orbitals of 1,3 dipoles and dipolarophiles. These generalizations were gleaned from calculations reported here as well as from experimental data available in the literature. In a recent communication[12] and in the following paper,[13] these generalizations are used as input into a general perturbation treatment of 1,3-dipolar cycloaddition reactivity, regioselectivity, and periselectivity.

Calculations. The calculations reported here were carried out by CNDO/2,[14] INDO,[14] or the extended Hückel (EH)[15] methods. Since the EH method is not an SCF method, it produces exaggerated charge distributions in molecules with heteroatoms such as the 1,3 dipoles. For this reason, details of the EH calculations are not given here, but some comparisons to be presented later will show that the CNDO/2 method and the EH method give the same qualitative trends and, in most but not all cases, the same generalizations can be made using either of these methods or other semiempirical or *ab initio* methods.

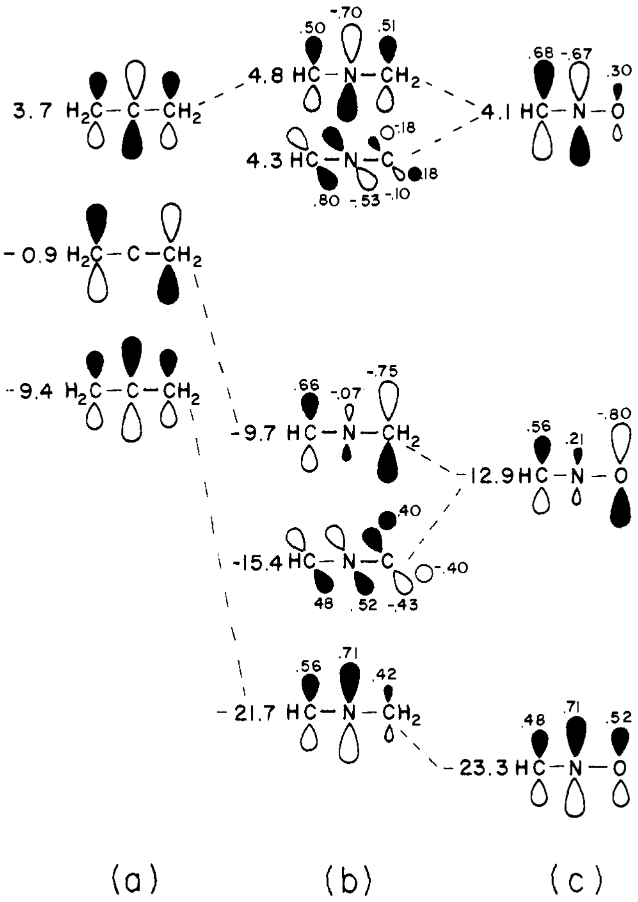

Figure 2. CNDO/2 π orbitals of (a) allyl anion, (b) formonitrile ylide, and (c) formonitrile oxide.

All 1,3 dipoles have in common a three atomic orbital π system containing four electrons analogous to an allyl anion. The relative energies of the frontier orbitals (highest occupied = HO; lowest unoccupied = LU) can be approximated from first-order perturbation theory. Figure 1 shows qualitatively the relative energies of the frontier π orbitals of the 1,3 dipoles. The HO and LU π orbitals of allyl anion are used as reference points and the change in energy upon heteroatom substitution is calculated as $\Delta E = \Sigma_r C_r^2 \Delta\alpha_r$,[16,17] where C_r is the Hückel coefficient for the HO or LU at position r, and $\Delta\alpha_r$ is the difference in valence state ionization potentials[18] between carbon and the heteroatom substituted at position r in the dipole. Since the HO of allyl anion has a node through the central atom, heteroatom substitution at this position will have no effect on energy to a first approximation, while terminal

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(8) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967).

(9) K. Fukui, *Bull. Chem. Soc. Jap.*, **39**, 498 (1966).

(10) K. N. Houk and C. R. Watts, *Tetrahedron Lett.*, 4025 (1970); K. N. Houk and L. J. Luskus, *ibid.*, 4029 (1970).

(11) R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968); *J. Chem. Soc. A*, 1570 (1970); *J. Org. Chem.*, **37**, 2181 (1972).

(12) K. N. Houk, *J. Amer. Chem. Soc.*, **94**, 8953 (1972).

(13) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Amer. Chem. Soc.*, accompanying paper.

(14) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, QCPE 141.

(15) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963); QCPE 64.

(16) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. Ser. A*, **191**, 39 (1947); **192**, 16 (1947); **193**, 447 (1948); **195**, 188 (1948).

(17) W. C. Herndon and W. B. Giles, *Mol. Photochem.*, **2**, 277 (1970).

(18) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962); a similar diagram appears in R. Sustmann, in press.

substitution will lower the HO energy to a large extent. By contrast, substitution at the central atom will have a larger lowering effect on the LU than terminal substitution. Since only the π systems are examined in Figure 1 without regard to geometry, the estimates for nitrilium betaines and azomethinium betaines are the same.

A more quantitative comparison of the allyl anion and two representative 1,3 dipoles, formonitrile ylide and formonitrile oxide (fulminic acid), is given in Figure 2. The allyl anion π MO's are derived from CNDO/2 calculations using 120° bond angles and a 1.40 Å bond length, while the 1,3-dipole calculations used minimum energy bond lengths (see later): formonitrile ylide, $r_{CH} = 1.09$ Å, $r_{CN} = 1.21$ Å, $r_{NC(H_2)} = 1.32$ Å; formonitrile oxide, $r_{CH} = 1.09$ Å, $r_{CN} = 1.21$ Å, $r_{NO} = 1.22$ Å. The sizes of the lobes of the 2p orbitals in this figure are roughly proportional to the coefficient at that position. Energies are given in eV.

Although the approximate nodal properties of the three allyl anion π MO's are preserved in the dipoles, the absolute energies of the bonding orbitals are lowered considerably by the electronegative N and O atoms in the 1,3 dipoles. The slightly increased energy of the dipole LU's as compared to the LU of the allyl anion may be attributed to the approximate cancellation of two factors: the shorter bond lengths and linearity of the dipole result in increased antibonding and decreased 1,3 bonding, respectively, tending to raise the LU energy, whereas the increased electronegativity of the atoms tends to lower the dipole LU energy.

In the "nonbonding" HO orbitals, the node is slightly displaced from the central atom, and from an orbital symmetry point of view, the analogy between allyl anion and 1,3 dipole MO's is adequate. However, the unequal magnitudes of the terminal coefficients in the HO and LU π orbitals of the dipoles are the keys to the explanation of regioselectivity in 1,3-dipolar cycloadditions.

The analogy of 1,3 dipole MO's to those of allyl anion does give an incorrect impression of the electron donor ability of 1,3 dipoles. The calculated energy of the HO orbital or formonitrile oxide (– 12.9 eV) is nearly identical to that of cyclopentadiene (– 13.0 eV), while the nitrile oxide LU energy (4.1 eV) is lower in energy than that of cyclopentadiene (4.6 eV). Thus, the calculations indicate that formonitrile oxide should be similar to a conjugated diene in electron donor properties and superior to a conjugated diene in its electron acceptor properties.

Since only the relative energies and atomic orbital coefficients of the frontier orbitals of a number of 1,3 dipoles were sought for input into a qualitative perturbation scheme, it was economical to perform calculations on the simplest 1,3 dipole models using standard geometries. However, in order to ensure that the eigenvalues and eigenvectors of 1,3 dipoles were not subject to gross changes upon slight geometrical variations, trial CNDO/2 calculations were performed on the formonitrile oxide and formonitrile ylide. In addition, INDO calculations were performed for formonitrile oxide with results very similar to CNDO/2. The distances were varied from 0.93 to 1.13 Å for CH, 1.00–1.39 Å for (H)CN, 1.00–1.35 Å for NO, and 1.20–1.35 Å for $NC(H_2)$.

Table II. Geometries Used in the Calculations[a]

Nitrilium Betaines [HCNX(H)]

X	r_{HC}	r_{CN}	r_{NX}	r_{XH}	$\angle$HCN	$\angle$CNX	$\angle$NXH
CH_2	1.09	1.21	1.32	1.08	180°	180°	120°
NH	1.09	1.21	1.27	1.00	180°	180°	120°
O	1.09	1.21	1.22		180°	180°	

Diazonium Betaines [NNX(H)]

X	r_{NN}	r_{NX}	r_{XH}	$\angle$NNX	$\angle$NXH
CH_2	1.11	1.32	1.08	180°	120°
NH	1.11	1.27	1.00	180°	120°
O	1.11	1.21		180°	

Azomethinium Betaines $[H_2CNHX(H)]$[b]

X	r_{HC}	r_{CN}	r_{NX}	r_{XH}	$\angle$HAB[c]	$\angle$CNX
CH_2	1.08	1.32	1.32	1.08	120°	120°
NH	1.08	1.32	1.27	1.00	120°	120°
O	1.08	1.32	1.21		120°	120°

Oxygenated Dipoles $[H_2COX(H)]$

X	r_{CH}	r_{CO}	r_{OX}	r_{XH}	$\angle$HAB[c]	$\angle$COX
CH_2	1.08	1.37	1.37	1.08	120°	120°
NH	1.08	1.37	1.32	1.00	120°	120°
O	1.08	1.37	1.27		120°	120°
Ozone			1.27			116°

[a] Lengths in Å, angles in degrees. [b] All $r_{NH^+} = 1.00$. [c] A, B = C, N, O.

For formonitrile oxide the following conclusions may be drawn from these calculations. (1) For the HO orbital, the coefficient at oxygen is always larger (30–110%) than that at carbon. Although the nitrogen coefficient varied, the node was invariably between the carbon and nitrogen. (2) For the LU orbital, the carbon coefficient was always considerably larger (100–220%) than that of oxygen, and the carbon and nitrogen coefficients were comparable in magnitude. (3) The HO orbital energies were relatively constant (– 12.8 ± 0.6 eV) while the LU orbital energies varied more appreciably (5.6 ± 1.7 eV) as the geometry was varied. (4) The calculated dipole moment varied from 3.15 to 4.96 D.

The calculated optimum geometry (linear, $r_{CH} = 1.09$ Å, $r_{CN} = 1.21$ Å, $r_{NO} = 1.22$ Å) and dipole moment (3.8 D) are only in moderate agreement with the structure of fulminic acid determined by microwave spectroscopy ($r_{HC} = 1.03$ Å, $r_{CN} = 1.16$ A, $r_{NO} = 1.21$ Å, $\mu = 3.1$ D)[19] and a recent CNDO/2 calculation ($r_{CN} = 1.19$ Å, $r_{NO} = 1.20$ Å).[20] MINDO/2 calculations give similar eigenvectors.[21]

For the formonitrile ylide, the coefficients and energies were more sensitive to geometrical variations. In the case of formonitrile ylide and similar C_{2v} dipoles, the LU is not the lowest vacant π orbital but is a pseudo-π orbital mainly localized between the (H)C and N atoms and lying in the molecular plane. Figure 2 shows orbitals of this type at 4.3 and – 15.4 eV. Variations in the nitrile ylide geometry gave results similar to those in Figure 2, except that in this case the larger terminal coefficient could be on either of the carbon termini in the HO or the LU. When the (H)CN bond length was longer than the $NC(H_2)$, the

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(19) K. Winnewisser and H. K. Bodenseh, *Z. Naturforsch. A*, **22**, 1724 (1967); H. K. Bodenseh and K. Winnewisser, *ibid.*, **24**, 1966, 1973 (1969).

(20) J. Bastide, N. El Ghandour, and O. Henri-Rousseau, submitted for publication.

(21) R. Sustmann, private communication.

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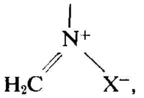
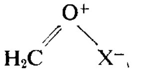
Table III. CNDO/2 Frontier Orbital Coefficients and Energies for 1,3-Dipoles

HC≡ N^+X^-,	NHO (in-plane)				HO (π)				LU (in-plane)				NLU (π)				π charges			Total charges			μ,
X	C_C	C_N	C_X	ε (eV)	C_C	C_N	C_X	ε (eV)	C_C	C_N	C_X	ε (eV)	C_C	C_N	C_X	ε (eV)	q_C	q_N	q_X	q_C	q_N	q_X	D
CH$_2$[a]	0.476	0.493	−0.443	−15.486	−0.643	0.066	0.763	−9.687	−0.789	0.545	0.103	4.370	−0.519	0.695	−0.498	4.901	−0.46	−0.03	−0.51	−0.15	+0.24	−0.26	2.03
NH[b]	0.470	0.249	−0.659	−13.064	−0.591	−0.051	0.801	−10.947	−0.722	0.601	−0.032	4.073	−0.597	0.695	−0.401	4.539	−0.29	−0.03	−0.68	−0.15	+0.32	−0.37	3.66
O[c]	0.560	0.208	−0.802	−12.895	−0.560	−0.208	0.802	−12.895	−0.677	0.673	−0.298	4.133	−0.677	0.673	−0.298	4.133	−0.08	−0.09	−0.82	−0.14	+0.37	−0.36	3.84
N≡N^+X^-, X	C_{N_1}	C_{N_2}	C_X	ε (eV)	C_{N_1}	C_{N_2}	C_X	ε (eV)	C_{N_1}	C_{N_2}	C_X	ε (eV)	C_{N_1}	C_{N_2}	C_X	ε (eV)	q_{N_1}	q_{N_2}	q_X	q_{N_1}	q_{N_2}	q_X	
CH$_2$[a]	0.487	0.454	−0.468	−16.852	−0.613	0.129	0.780	−11.047	−0.763	0.567	0.114	4.340	−0.497	0.704	−0.507	4.468	−0.51	−0.01	−0.49	−0.14	+0.31	−0.26	0.73
NH[b]	0.456	0.228	−0.711	−14.354	−0.562	0.013	0.827	−12.364	−0.709	0.622	−0.050	3.850	−0.579	0.708	−0.405	4.133	−0.33	+0.00	−0.67	−0.13	+0.40	−0.37	1.89
O[c]	0.542	0.138	−0.829	−14.482	−0.542	−0.138	0.829	−14.482	−0.651	0.693	−0.310	3.725	−0.651	0.693	−0.310	3.725	−0.15	−0.04	−0.81	−0.14	+0.47	−0.33	0.98
 X					C_C	C_N	C_X	ε (eV)					C_C	C_N	C_X	ε (eV)	q_C	q_N	q_X	q_C	q_N	q_X	
CH$_2$[a]					−0.705	0	0.705	−8.998					−0.532	0.659	−0.532	3.491	−0.43	−0.13	−0.43	−0.21	+0.23	−0.21	2.27
NH[b]					−0.669	−0.071	0.740	−10.185					−0.583	0.668	−0.463	3.165	−0.32	−0.11	−0.57	−0.16	+0.29	−0.34	4.05
O[b]					−0.654	−0.155	0.740	−11.455					−0.618	0.674	−0.406	2.939	−0.24	−0.09	−0.67	−0.13	+0.34	−0.38	3.65
 X					C_C	C_O	C_X	ε (eV)					C_C	C_O	C_X	ε (eV)	q_C	q_O	q_X	q_C	q_O	q_X	
CH$_2$[a]					−0.707	0	0.707	−9.254					−0.563	0.604	−0.563	1.212	−0.37	−0.27	−0.37	−0.10	+0.10	+0.10	0.20
NH[b]					−0.634	−0.081	0.769	−10.424					−0.640	0.614	−0.463	0.776	−0.18	−0.25	−0.57	−0.01	+0.13	−0.27	2.20
O[b]					−0.564	−0.190	0.804	−11.910					−0.710	0.610	−0.354	0.370	+0.01	−0.26	−0.75	+0.06	+0.15	−0.34	4.01
Ozone					−0.707	0	0.707	−14.636					−0.525	0.669	−0.525	−1.614	−0.45	−0.10	−0.45	−0.16	+0.31	−0.16	1.20

[a] C_{2v}: NHO, LU = b_1; HO, NLU = b_2. [b] C_s: NHO, LU = a′; HO, NLU = a″. [c] $C_{\infty v}$: NHO, HO = π_x, π_y (degenerate); NLU, LU = π_x^*, π_y^* (degenerate).

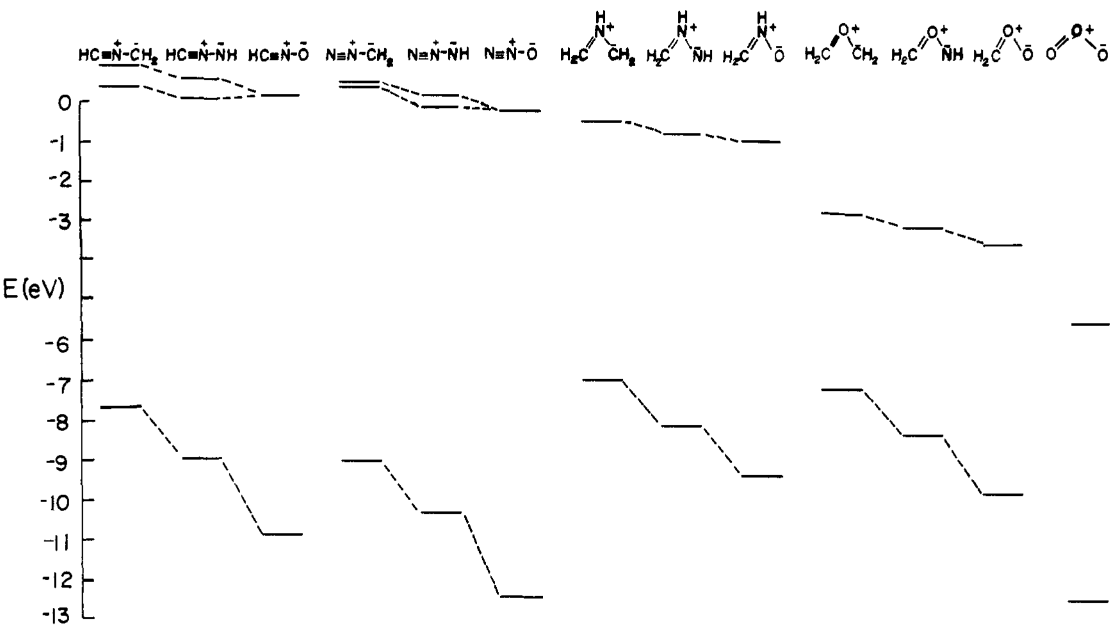


Figure 3. CNDO/2 frontier orbital energies for 1,3-dipoles ($\epsilon_{HO} = \epsilon_{calcd} + 2eV$; $\epsilon_{LU,NLU} = \epsilon_{calcd} - 4eV$).

larger coefficient was on (H)C in the HO and on $C(H_2)$ in the LU. When the relative bond length relationship was reversed, the position of the larger frontier orbital coefficient was reversed. Changes in CH bond lengths left the π orbital energies and coefficients essentially unchanged.

Our conclusion from these calculational experiments is that the qualitative shapes of the 1,3-dipole frontier orbitals are rather insensitive to geometrical variations unless the two terminal atoms are the same. For this reason, geometrical variations were not attempted for other 1,3 dipoles, but the set of bond lengths and angles in Table II was adopted.

Having shown some of the gross features of 1,3 dipole π MO's, the orbitals of a whole series of 1,3 dipoles can be examined. The CNDO/2 coefficients and energies of the frontier orbitals are shown in Table III and Figure 3. For purposes of comparison with later "empirical" values of orbital energies, the energies plotted in Figure 3 result from adding 2 e V to the HO energies of Table III, and – 4 eV to the LU and NLU energies of Table III. For the dipoles of $C_{\infty v}$ symmetry (HCNO, NNO), the HO and LU orbitals occur as pairs of degenerate π orbitals. For those dipoles "with a double bond" which have C_{2v} [$HCNCH_2$, H_2CNN) or C_s (HCNNH, NNNH) symmetry, the NHO (next to HO) and LU orbitals lie in the plane of the molecule. Figure 4 shows the EH frontier orbital energies for some of the dipoles. The trends in Figures 3 and 4 can be seen to be qualitatively similar and conform to the trends of Figure 1.

The energy diagrams suggest a generalization about the relative reactivities of the different 1,3 dipoles. Perturbation theory, which will be applied to these reactions in detail in the following paper, indicates that reactivity in cycloadditions will increase as the dipole LU orbital is lowered and as the HO orbital is raised in energy. Since the changes in LU orbital energies parallel, but are less than, those of the HO orbital in the 1,3 dipole series, the energy of the HO orbital gives a rough index to the reactivity of the 1,3 dipoles. Thus,

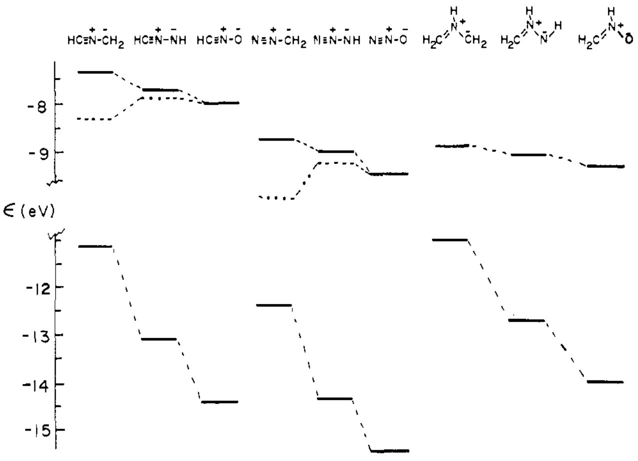


Figure 4. EH frontier orbital energies for 1,3 dipoles.

nitrile ylides can be prepared only as transient intermediates, nitrile imines as less reactive transient intermediates, and nitrile oxides as less reactive compounds which are often isolable or dimerize slowly.

In the diazonium betaine series, diazoalkanes are isolable species which react with most alkenes at 0°, azides react with alkenes upon heating, and nitrous oxide is quite unreactive, requiring temperatures in excess of 200° and pressures of several hundred atmospheres for reaction with alkenes to occur.

In comparing the nitrilium betaines and the diazonium betaines, diazoalkanes are on the same order of reactivity as nitrile oxides, while azides are less reactive than nitrile oxides.

In the azomethinium betaine series, azomethine ylides can be generated as transient intermediates when electron-withdrawing groups are attached to the carbons, azomethine imines react readily with dipolarophiles or dimerize reversibly, and nitrones are isolable compounds whose reactivity with alkenes falls somewhere between diazoalkanes and azides. The approximate relative reactivities of 1,3 dipoles are well

Table IV. CNDO/2 HO and LU π and In-plane Molecular Orbital Coefficients and Energies for Nitrile Oxides

Nitrile oxide (RCNO), R	NHO (in-plane)				HO (π)				LU (π)			
	C_C	C_N	C_O	ϵ (eV)	C_C	C_N	C_O	ϵ (eV)	C_C	C_N	C_O	ϵ (eV)
H[a]	0.560	0.208	−0.802	−12.895	−0.560	−0.208	0.802	−12.895	0.677	−0.673	0.298	4.133
Me[b]	0.524	0.257	−0.764	−11.954	−0.524	−0.257	0.764	−11.954	0.604	−0.627	0.284	4.052
Ph[c]	0.457	0.362	−0.688	−12.090	−0.438	−0.308	0.602	−11.028	0.326	−0.477	0.253	2.193

Nitrile oxide (RCNO), R	NLU (in-plane)				μ, D	Charges, π			Charges, total		
	C_C	C_N	C_O	ϵ (eV)	Calcd (exptl)	q_C	q_N	q_O	q_C	q_N	q_O
H[a]	−0.677	0.673	−0.298	4.133	3.84 (3.06)	−0.08	−0.09	−0.82	−0.14	+0.37	−0.36
Me[b]	−0.604	0.627	−0.284	4.052	4.45 (4.50)	−0.06	−0.13	−0.83	−0.06	+0.31	−0.37
Ph[c]	−0.691	0.606	−0.243	4.680	5.21 (4.00)	−0.08	−0.12	−0.80	−0.07	+0.21	−0.41

[a] $C_{\infty v}$: NHO, HO = π_x, π_y; LU, NLU = π_y^*, π_x^*. [b] C_{3v}: HO, LU lie in plane (σ_{yz}) containing one hydrogen; NHO, NLU lie in plane perpendicular to σ_{yz}. [c] C_{2v}: HO, LU = b_2 (perpendicular to molecular plane); NHO, NLU = b_1 (in molecular plane).

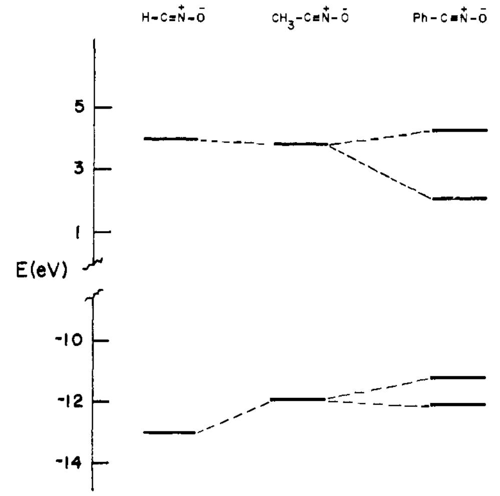


Figure 5. CNDO/2 frontier orbital energies of substituted nitrile oxides.

accounted for by the relative HO orbital energies of Figures 1, 3, and 4. This gross generalization is the first indication that the calculations give reactivity trends which are compatible with a perturbation treatment of 1,3-dipole reactivity.

The coefficients of different atomic orbitals will serve as a starting point for the perturbation treatment of reactivity. As shown in Table III, qualitative generalizations may be made about the shapes of the eigenvectors in each type of frontier orbital.

Thus, the HO orbital in each of these 1,3 dipoles has the largest coefficient on the "anionic" atom, except in the case of the symmetrical (C_{2v}) dipoles. The negative charge on the "anionic" atoms in the resonance structures in the first column of Table I is representative of the predominant polarization shown by the calculated total charges in Table III. However, in the 1,3 dipoles with a central nitrogen atom, both ends of the 1,3 dipole bear substantial negative charges (−0.14 to −0.21 for the "neutral" atom, −0.21 to −0.40 for the "anionic" atom), while the central nitrogen is positively charged (+0.23 to +0.47). The π charges listed in Table III exaggerate the amount of negative charge borne by the "anionic" atom, since these are all calculated with reference to $C_r^2 = 1$ for $q = 0$. The carbonyl betaines have less symmetrical charge distributions but the trends are similar.

The lowest unoccupied orbitals of the six "octet stabilized 1,3 dipoles with a double bond" are in-plane orbitals consisting mainly of a π^* orbital joining the "triply bonded" atoms. In each of these orbitals, as well as in the NLU π orbitals, the largest coefficient is on the "neutral" terminal atom. Diazomethane is the sole exception since the thermal NLU coefficients are virtually identical.

Many 1,3-dipolar cycloaddition studies have used heavily substituted 1,3 dipoles as addends, and, indeed, substituents on the 1,3 dipole are known to influence the reactivity and regioselectivity of the 1,3 dipole. In order to test the effect of substituents on the molecular orbitals of 1,3 dipoles, trial calculations were performed on a series of nitrile oxides. The results of these CNDO/2 calculations are shown in Table IV and Figure 5. For formonitrile oxide, the heavy lines represent the degenerate HO and LU π orbital energies in the calculated minimum energy geometry, and for acetonitrile oxide, the HO and LU orbitals are each a degenerate pair of orbitals, whereas this degeneracy is split in benzonitrile oxide. Table IV gives frontier orbital coefficients and energies, the π and total charges, and the calculated and experimental[22] dipole moments. The geometries used for these calculations were the same as those in Table II for the nitrile oxide fragment, with standard bond angles and lengths[14] for the methyl and phenyl fragments.

Methyl substitution (acetonitrile oxide (C_{3v}) results in a slight compression of the separation between HO and LU orbitals which results from mixing of the occupied dipole orbitals with lower-lying bonding CH orbitals in an antibonding fashion. The frontier orbital separation is further narrowed in benzonitrile oxide. The HO and LU orbitals of this species are π orbitals (perpendicular to the plane of the molecule) which are compressed due to mixing with the symmetric π and π^* orbitals of the aromatic rings. The in-plane dipole π orbitals are less affected by aryl substitution. The compression of frontier orbitals should result in augmented reactivity, although steric effects of bulky substituents may counterbalance this activation effect.

Inspection of Table IV reveals that the nodal positions and relative magnitudes of the atomic orbital coefficients are preserved in formonitrile oxide and its substituted derivatives. However, the difference in the terminal coefficients in the nitrile oxide HO decreases as the nitrile oxide becomes more heavily substituted.

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(22) Ch. Grundmann and P. Grunanger, "The Nitrile Oxides," Springer-Verlag, Heidelberg, 1971, and references therein.

Thus, for a parent 1,3 dipole such as formonitrile ylide, in which the terminal coefficients are more nearly equal, substitution may reverse the relative magnitudes of terminal coefficients. With this exception, these calculations indicate that qualitative perturbation treatments based on molecular orbitals of a parent 1,3 dipole should also be valid for substituted derivatives, and, furthermore, that both π and total charges are only slightly affected by substitution.

Comparisons between calculations for the pairs diazomethane and vinyldiazomethane, azomethine imine and sydnone, and a number of substituted nitrones lead to similar conclusions about the relative insensitivity of eigenvectors to substitution.

The nitrile ylides present a special case due to the near identity of the HO orbital coefficients. Attachment of an alkyl or aryl group to an alkene π system makes the coefficient at the point of attachment lower than the remote coefficient in the HO (see later discussion of dipolarophiles). This effect can be seen for the nitrile oxide calculations and will have the possible consequence of reversing the relative frontier orbital coefficient magnitudes in the HO of nitrile ylides from those given in Table III and making the HO terminal coefficients more nearly the same in the nitrile imines.[22a]

A further geometrical variation was explored for its effect on CNDO/2 eigenvalues and eigenvectors. It has been proposed that the transition states of 1,3-dipolar cycloadditions of linear 1,3 dipoles to alkenes involve appreciable bending of the 1,3 dipole.[5] Such a complex would maximize overlap of the p orbitals at the termini of the dipole with those of the dipolarophile. The perturbation calculation of regioselectivity based on linear 1,3 dipole MO's could be in serious error were the bent and linear dipole MO's significantly different.

Roberts performed Hückel calculations on azides which indicated that bending the NNN angle below 180° would require little energy.[23] Calculations carried out here by the CNDO/2 method for diazomethane using fixed bond lengths but with variations of the CNN angle in the plane of the molecule from 180° to 120° show that bending causes only small changes in the coefficients and energies of the HO and LU π orbitals. In all cases, the relative magnitudes of coefficients remain the same, indicating that the calculations of linear systems are satisfactory for perturbation predictions even if the transition state involves a substantially bent 1,3 dipole. The calculations indicate a substantial energy barrier to in-plane bending of the CNN angle. Decreasing this angle from 180° to 150° causes an increase in energy of 14 kcal/mol, while bending to 120° causes an energy increase of 34 kcal/mol. These bending energies are undoubtedly too high, since geometry optimization was not carried out at each angle of bend. However, it appears unlikely that any appreciable bending of the 1,3 dipole occurs before substantial bonding between 1,3 dipole and dipolarophile takes place, since activation energies of 5–15 kcal/mol are common for diazoalkane 1,3-dipolar cycloadditions.[24] Calculations of a similar nature have recently been reported by Bastide and Henri-Rousseau.[25] These authors found that bending to 109° required 63 kcal/mol when bond lengths were not reoptimized. A barrier of 22.3 kcal/mol resulted at 109° when bond angles were reoptimized, and a minimum at 75° (8.3 kcal/mol more stable than the 180° geometry!) was found.[25]

Having briefly surveyed the trends in dipole frontier orbital energies and coefficients as a function of heteroatom constituents and geometrical variations, the major task of this work, the construction of an experimentally reasonable set of these quantities, can now be broached. The discussion of orbital energies has been confined so far to relative considerations and for good reason: first, CNDO/2 calculations, as well as other semiempirical calculation schemes, do not give reliable orbital energies as measured by photoelectron spectroscopy,[26,27] although relative orbital energies are often satisfactory if a suitably narrow range of compounds is compared; and second, the same or greater difficulties may be expected to occur in calculations of electron affinities from LU orbital energies. Thus, we will endeavor, wherever possible, to assign frontier orbital energies from experimental data, using calculations only as a guideline or to fill in where no experimental data are available.

The HO orbital energy will be derived from ionization potential data obtained from photoelectron spectra. Assuming Koopmans' theorem, the ionization potential is the negative of the orbital energy.[27] Where ionization potentials are not available, extrapolations are made with the aid of the calculations reported here. The LU orbital energy is set equal to the negative of the electron affinity of the molecule. Unfortunately, these data are almost nonexistent for the dipoles and for many alkenes, so approximations are made from spectroscopic data or from calculations, since linear correlations between $-\epsilon_{LU}$ and EA have been found for SCF calculations on a variety of molecules.[28] Calculations involving reminimization of the radical anion energy that indicate errors of similar magnitude are involved in the application of Koopmans' theorem to the estimation of IP's and EA's.[29]

Further aid in assignment of LU energies can be obtained from reduction potentials and charge transfer energies. Various correlations of these types of data with electron affinities indicate that relative changes in LU orbital energies may be determined in this way.[30]

In a similar series of molecules, the relative but not absolute energies of the LU orbitals can be reasonably approximated from uv spectral data. The validity of this approach can be seen empirically from recent linear correlations of reduction potentials with $\pi\pi^*$ triplet energies in unsaturated ketones.[31,32] Transitions to

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(22a) NOTE ADDED IN PROOF. The "reversal" of nitrile ylide HO coefficients suggested here has been experimentally deduced from the site of electrophilic attack on substituted nitrile ylides: A. Padwa and J. Smolanoff, *J. Chem. Soc., Chem. Commun.*, 342 (1973).

(23) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1962, p 131ff.

(24) G. W. Cowell and A. Ledwith, *Quart. Rev. Chem. Soc.*, 24, 119 (1970); A. Ledwith and D. Parry, *J. Chem. Soc. C*, 1408 (1968).

(25) J. Bastide and O. Henri-Rousseau, *Tetrahedron Lett.*, 2979 (1972).

(26) S. D. Worley, *Chem. Rev.*, 71, 295 (1971).

(27) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970: (a) p 61 ff; (b) p 86 ff; (c) p 166 ff; (d) 168 ff; (e) p 250; (f) p 22 ff; (g) p 170 ff.

(28) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, 36, 21 (1962).

(29) T. L. Kunii and H. Kuroda, *Theor. Chim. Acta*, 11, 97 (1968).

(30) G. Briegleb, *Angew. Chem., Int. Ed. Engl.*, 3, 617 (1964).

(31) R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, 50, 4050 (1972).

(32) W. E. Wentworth and E. Chen, *J. Phys. Chem.*, 71, 1929 (1967).

singlet excited states involving promotion of an electron from a filled orbital, i, to a virtual orbital, j, are calculated by SCF methods from the following expression

$$\Delta E = \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij}$$

where ϵ_i and ϵ_j are the orbital energies and J_{ij} and K_{ij} are the Coulomb and exchange integrals, which account for differences in electron repulsion in the ground and excited states.[33] Evaluation of J and K is carried out in the CNDO approximation from the coefficients of i and j and the distances between atoms, as well as from calculated or approximated electron repulsion integrals. Thus, for a series of similar molecules such as substituted alkenes, $-J_{ij} + 2K_{ij}$ ($\equiv -\Delta$) for $\pi\pi^*$ transitions will be approximately constant, since the coefficients of MO's i or j, as well as the distance between atoms, will remain approximately constant. For example, the $\pi\pi^*$ transition of ethylene is at 7.7 eV, while the estimated electron affinity (see later) is -1.5 eV ($\epsilon_{LU} = +1.5$ eV). Thus, Δ can be estimated as 4.3 eV for ethylene, using the negative of the ionization potential (10.5 eV) as the HO orbital energy. For acrolein, the ionization potential of 10.9 eV, $\pi\pi^*$ transition energy of 5.95 eV, and estimated electron affinity (see later) of 0.0 eV give a value of $\Delta =$ 4.9 eV. Even these cases, which are particularly unfavorable cases due to the greater delocalization and presence of a heteroatom in acrolein, still give reasonably close values of electron repulsion changes. For a series of alternate aromatic hydrocarbons, Δ has been found to have the relatively constant value of 3.4–3.8 eV.[34]

For the 1,3 dipoles, HO and LU coefficients do not change drastically along the series, so Δ may remain relatively constant. Electron repulsion integrals increase along a series of atoms of increasing electronegativity due to orbital contraction, but since these integrals are involved in both J and K, the differences induced by heteroatoms may not be inordinately large. The only 1,3 dipole for which electron affinity, ionization potential, and electronic absorption data are all known is ozone. These data can be used to empirically estimate Δ for 1,3 dipoles.

Ozone has an electron affinity of about 2.2 eV ($\epsilon_{LU} = -2.2$ eV),[35] σ and π ionization potentials of 12.52 and 13.5 eV, respectively,[27b] and $\sigma\pi^*$ and $\pi\pi^*$ singlet–singlet transitions of 2.1 and 3.5 eV, respectively.[36] For the $\sigma\pi^*$ transition, $\Delta = 12.52 - 2.2 - 2.1 \cong 8.2$ eV, while for the $\pi\pi^*$ transition, $\Delta = 13.5 - 2.2 - 3.5 \cong 7.8$ eV. The Δ's calculated for ozone are much larger than those calculated for alkenes. This difference can be attributed both to the greater electronegativity and thus greater magnitude of the electron repulsion integrals[37] of ozone as compared to an alkene. For dipoles made up of less electronegative atoms which are also linear, Δ is expected to be smaller. We have chosen the values of Δ for $\sigma\pi$ and $\pi\pi$ transitions to be close to those of alkenes, that is, 6.0 and 5.0 eV, respectively. This crude approximation is used to obtain ϵ_{LU} for dipoles for which no electron affinity data are available.

Diazoalkanes. In addition to those reported here, recent calculations by the EH,[38] Mulliken–Wolfsberg–Helmholz (MWH),[39] ASMO–SCF,[40] CNDO/2,[25] and *ab initio*[41] methods have been reported for diazoalkanes. The charge densities and relative magnitudes of the frontier orbital coefficients are given by Bastide, *et al.*,[20] and agree with those reported in Table III. The *ab initio* results differ from CNDO/2 in that the C_1, N_2, and N_3 total charges are -0.46, -0.03, and $+0.03$, respectively.[41] The experimental ionization potential of diazomethane is 8.99 eV,[42] considerably lower than that calculated by any of the semiempirical methods. The electron affinity of diazomethane and thus the LU and NLU energies are not known but can be estimated from spectroscopic data.

The two lowest transitions observed in the absorption spectrum of diazomethane at 3.14 and 5.77 eV have been assigned to $\pi\sigma^*$ [HO $\rightarrow$ LU (in-plane)] and $\pi\pi^*$ (HO $\rightarrow$ NLU) transitions,[39,40] respectively, where the designations used here correspond to those in Table III. For the HO $\rightarrow$ NLU or $\pi\pi^*$ transition, we will use a Δ of 5.0 eV to estimate the NLU energy. Thus, the NLU or π^* orbital of diazomethane is estimated to lie at $-8.99 + 5.77 + 5.0 \cong +1.8$ eV. The LU is expected to lie at lower energy from calculations reported here and elsewhere. For a "$\pi\sigma$"-type transition such as the HO $\rightarrow$ LU transition at 3.14 eV in diazomethane, the larger Δ of 6 eV is used, since K is small for transitions between orbitals which do not overlap much. The crude estimate of the diazomethane LU energy is: $-8.99 + 3.17 + 6.0 \cong +0.2$ eV.

Hydrazoic Acid. Calculations on hydrazoic acid and alkyl azides by MWH,[43] HMO,[44] CNDO/2 (phenyl azide),[20] and *ab initio*[45] methods have been reported. The level ordering and eigenvectors[43] in these published results are in general agreement with those reported here. The first ionization potential of hydrazoic acid, measured from the Rydberg spectra, is 11.5 eV, while the $\pi\sigma^*$ (HO $\rightarrow$ LU) and $\pi\pi^*$ (HO $\rightarrow$ NLU) (Table III designations) are assigned to bands at 4.70 and 6.56 eV.[43] Using the values for Δ of 6.0 and 5.0 eV determined previously for these transitions leads to ϵ_{LU} (in-plane) $-11.5 + 4.7 + 6.0 = -0.8$ eV and ϵ_{NLU} (π^*) $= -11.5 + 6.6 + 5.0 = +0.1$ eV.

The absorption spectrum of n-amyl azide has the corresponding absorption bands at 4.31 and 6.50 eV.[44] Most of this difference probably arises from raising the HO by alkyl substitution, as will be discussed in more detail in the section on substituent effects.

Nitrous Oxide. Calculations by MWH,[36] variously parameterized EH and CNDO,[46] and *ab initio*[47] meth-

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[33] For a general discussion with definitions, see H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, 47, 792 (1967).

[34] J. Michl and R. S. Becker, *J. Chem. Phys.*, 46, 3889 (1967).

[35] H. O. Pritchard, *Chem. Rev.*, 52, 529 (1953).

[36] H. J. Maria, D. Larson, M. E. McCarville, and S. P. McGlynn, *Accounts Chem. Res.*, 3, 368 (1970).

[37] See, for example, R. L. Flurry, Jr., "Molecular Orbital Theories of Bonding in Organic Molecules," Marcel-Dekker, New York, N. Y., 1968, p 222 ff.

[38] R. Hoffmann, *Tetrahedron*, 22, 539 (1966).

[39] J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, 71, 73 (1971).

[40] Z. Yoshida and T. Kobayashi, *Bull. Chem. Soc. Jap.*, 45, 742 (1972); Z. Yoshida and T. Kobayashi, *J. Chem. Phys.*, 58, 334 (1973).

[41] J.-M. Andre, M. C. Andre, G. Leroy, and J. Weiler, *Int. J. Quantum Chem.*, 3, 1013 (1969).

[42] G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Toronto, Can., 1967.

[43] J. R. MacDonald, J. W. Rabalais, and S. P. McGlynn, *J. Chem. Phys.*, 52, 1332 (1970).

[44] W. D. Closson and H. B. Gray, *J. Amer. Chem. Soc.*, 85, 290 (1963).

[45] R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, 48, 1500 (1968).

ods have been reported. In the case where eigenvectors have been reported,[36] good agreement of relative coefficient magnitudes with those listed in Table III is found. An experimental ionization potential of 12.89 eV has been reported for nitrous oxide.[27a] Transitions involving the degenerate HO and LU orbitals give rise to singlet–singlet absorptions at 4.54, 6.81, and 9.66 eV.[36] Independent estimates of the LU energies may be obtained using the first two bands, which correspond to transition of the type that have $\Delta = 6.0$ and 5.0 eV, respectively. Thus, $\epsilon_{LU} = -12.89 + 4.54 + 6.0 \cong -2.4$ or $-12.89 + 6.81 + 5.0 \cong -1.1$ eV. In light of the experimental electron affinities of ozone and NO_2 of 2.2 and 1.6 eV,[35] respectively, the latter estimate for ϵ_{LU} seems preferable.

Ozone. Numerous calculations on the ozone molecule have been performed, including several recent *ab initio*[48] as well as MWH[36] calculations. These calculations as well as the EH calculations performed here indicate the HO is a b_1 (C_{2v}) σ orbital, while the highest π orbital (a_2) is lower in energy. The CNDO/2 calculations performed here indicate that the latter is the HO. The LU is the a_1 π^* orbital in all calculations. The $\sigma\pi^*$ ($b_1 \rightarrow a_1$) and $\pi\pi^*$ ($a_2 \rightarrow a_1$) transitions in ozone occur at 2.1 and 3.5 eV.[36] The photoelectron spectrum of ozone has vertical ionizations at 12.52 and 13.5 eV, which have been assigned to ionizations from σ and $a_2(\pi)$ orbitals, respectively.[27b] If these ionization potentials are assigned to the b_1 and a_2 ionizations, independent estimates of the π^* energy of $\epsilon_{LU} = -12.52 + 6.0 + 2.1 = -4.4$ eV and $-13.5 + 5.0 + 3.5 = -5.0$ eV can be made. Of course, the Δ for ozone was calculated earlier and this exercise is only to show the degree of disagreement which might be expected in the limits of the approximation used here. As mentioned previously, one measurement of the electron affinity gave a value of roughly 2.2 eV,[36] while a more recent measurement has set a lower limit of 1.96 eV on the ozone electron affinity.[49]

Carbonyl Betaines. Very little data are available on the carbonyl ylides or oxides, but since they resemble ozone more closely than other dipoles, frontier orbital energy estimates can be made. Using the method used to produce Figure 1, carbonyl oxide is expected to have its HO and LU destabilized by 3.2 and 1.3 eV, respectively, relative to ozone. Thus, HO(π) and LU(π) energies of -10.3 and -0.9 eV are estimated. From this crude estimate, carbonyl oxides, which are well known intermediates in the ozonolysis mechanism, should resemble hydrazoic acid but should be somewhat better electron donors.

A similar estimate (Figure 1) for carbonyl ylide gives $\epsilon_{HO} = -7.1$ eV and $\epsilon_{LU} = +0.4$ eV. The parent system is expected to be more nucleophilic than diazomethane. Hayes has performed *ab initio* calculations on the parent carbonyl ylide.[50] These calculations indicate that the planar form is somewhat more stable than one with terminal methylenes rotated by 90°. Both of these geometries are less stable than the closed ethylene oxide form.

Nitrile Oxides. In addition to those reported here, nitrile oxide calculations by HMO,[51] CNDO/2,[20] and MINDO/2[21] methods have been reported. These calculations all have in common the feature noted in Tables III and IV; namely, the HO orbital has the larger terminal coefficient on oxygen, whereas the NLU(π^*) has a much larger coefficient on carbon than on oxygen.

No ionization potential data for fulminic acid or its substituted derivatives have been reported, so that estimates must once again be made. Electronegativity considerations indicate that the HO and LU π orbitals of formonitrile oxide (fulminic acid) should be destabilized by 1.54 and 0.64 eV with respect to the corresponding orbitals of nitrous oxide, leading to estimates of $\epsilon_{HO} = -11.4$ eV and $\epsilon_{LU}(\pi) = -0.5$ eV. A similar estimate using diazomethane as reference gives $\epsilon_{HO} = -10.6$ eV and $\epsilon_{LU} = +1.1$ eV. Sustmann has carried out unpublished MINDO/2 calculations which indicate that $\epsilon_{HO} = -10.69$ eV and $\epsilon_{LU} = -0.39$ eV.[21]

For the purposes of the qualitative theory, the "average" values of -11.0 and -0.5 eV have been adopted for the HO and LU orbital energies. For comparison, the CNDO/2 calculations listed in Table III predict HO energies of -12.99 and -11.05 eV for formonitrile oxide and diazomethane, both values of which are 2 eV lower than the HO energies estimated here.

Although rather extensive studies of the absorption spectra of arylnitrile oxides have been carried out,[22,51] no data on formonitrile oxide are available to confirm the estimates made here.

Nitrile Imines and Ylides. These species are known only as rather heavily substituted derivatives, and no spectroscopic data are available. We have chosen the expediency of using electronegativity estimates extrapolated from the adopted values for formonitrile oxide (first number below) or using the CNDO/2 calculated orbital energies for HO and LU estimates. In the latter case, ${\epsilon_{HO}}^{est} = {\epsilon_{HO}}^{CNDO/2} + 2$ eV and ${\epsilon_{NLU(\pi)}}^{est} = {\epsilon_{NLU(\pi)}}^{CNDO/2} - 4.6$ eV; that is, the nitrile oxide estimates were used as a reference point. The results are shown for both estimates and the average is given in parentheses: ϵ_{HO} (nitrile imine), -9.4, -9.0 (-9.2), and $\epsilon_{LU(\pi)}$, $+0.2$, -0.1 ($+0.1$); ϵ_{HO} (nitrile ylide), -7.8, -7.7 (-7.7), and $\epsilon_{NLU(\pi)}$, $+1.5$, $+0.3$ ($+0.9$).

Having roughly equal faith in the qualitative and more elaborate CNDO/2 approximations, we will use the average values listed in parentheses in future discussions. Bastide, *et al.*, performed CNDO/2 calculations on diphenylnitrile imine which confirm the coefficient magnitudes reported in Table III.[20]

Nitrones. Although the parent nitrone, a tautomer of formaldoxime, has been trapped in cycloadditions, no spectral data are available on this compound. Of the numerous stable substituted derivatives, we have measured the photoelectron spectra of *N-tert*-butylmethylenenitrone and *C*-phenyl-*N*-methylnitrone and have carried out CNDO/2 calculations on substituted systems in addition to the parent. The lowest vertical

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(46) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **11**, 239 (1968).

(47) A. D. McLean and M. Yoshimine, "Tables of Linear Molecular Wave Functions," IBM, San Jose, Calif., 1967, referred to in ref 35; M. Yoshimine and A. D. McLean, *Int. J. Quantum Chem.*, **1S**, 313 (1967).

(48) C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, 48, 407 (1968); S. D. Peyerimhoff and R. J. Buenker, *ibid.*, 47, 1953 (1967); E. F. Hayes and A. K. Q. Siu, *J. Amer. Chem. Soc.*, 93, 2090 (1971).

(49) J. Berkowitz, W. A. Chupka, and D. Gutman, *J. Chem. Phys.*, **55**, 2733 (1971).

(50) E. F. Hayes, *ibid.*, **51**, 4787 (1969).

(51) M. Yamakawa, T. Kubota, H. Akazawa, and I. Tanaka, *Bull. Chem. Soc. Jap.*, 41, 1046 (1968); M. Yamakawa, T. Kubota, and H. Akazawa, *ibid.*, **40**, 1600 (1967).

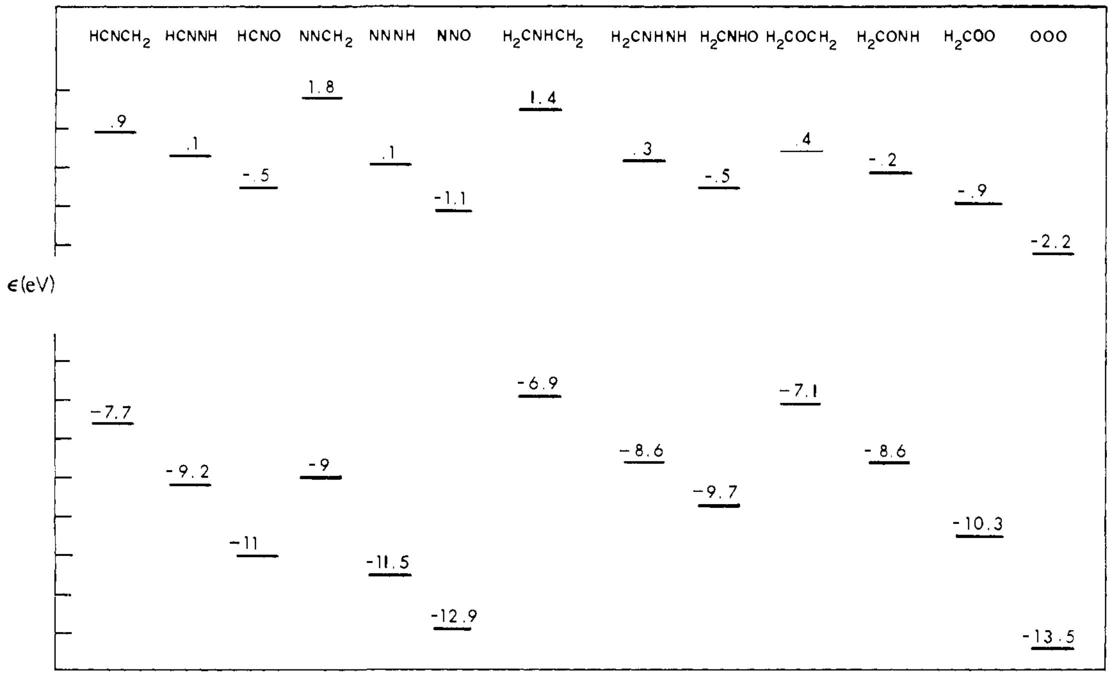

Figure 6. Estimated π frontier orbital energies for the 1,3 dipoles.

ionization potentials of the *N-tert*-butylmethylenenitrone at 8.64 and 9.07 eV have been assigned to ionization from the π and n (mainly on oxygen) orbitals, respectively.[52] The absorption spectrum of this nitrone shows a strong band at 5.16 eV.[53] Extensive studies of various *C*-aryl-*N*-alkylnitrones have led to the assignment of the band at 4.23 eV (*n*-heptane) in *C*-phenyl-*N*-methylnitrone to the $\pi\pi^*$ (HO $\rightarrow$ LU, Table III) transition.[54] Thus, assuming the 5.16 eV band in the *N-tert*-butyl compound is due to a $\pi\pi^*$ transition and 8.64 eV represents the π ionization, and using a value of 4 eV for Δ, a LU energy estimate of $-8.64 + 5.16 + 4 = +0.5$ eV can be made for *N-tert*-butylnitrone. As the discussion of substituent effects will show, this leads to estimates of $\epsilon_{\mathrm{HO}} = -9.7$ eV and $\epsilon_{\mathrm{LU}} = -0.5$ eV for the parent nitrone system. The reduced vlaue of Δ was chosen here since the bond lengths in the nitrone are considerably longer than those in nitrile oxides so that two-center electron repulsions should be decreased, and also to bring the HO and LU energies of these compounds into line with expectations based on the difference between alkenes and alkynes[51] (see dipolarophile discussion). The resulting estimates are in qualitative agreement with calculations (*cf.* Table III).

Azomethine Imines and Ylides. Once again, a paucity of experimental data prevents the accurate empirical estimation of frontier orbital energies. As in previous discussions, estimates based on extrapolations from nitrone values using electronegativity changes (first number below), from CNDO/2 energy changes (second number), or from extrapolations from hydrazoic acid and diazomethane energies using CNDO/2 energy charges (third number) are (in eV): ϵ_{HO} (azomethine imine), -8.1, -8.4, -9.3 (-8.6), and ϵ_{LU}, $+0.2$, $+0.6$, 0.0 ($+0.3$); ϵ_{HO} (azomethine ylide), -6.5, -7.2, -7.0 (-6.9), and ϵ_{LU}, $+0.8$, $+0.7$, $+2.8$ ($+1.4$). Once again the average values (given in parentheses) will be used in future discussions.

Summary of Parent Dipole Energies. The results of the previous considerations are summarized in Figure 6. Comparison of Figure 6 with Figures 1, 3, and 4 reveals close similarities. Of course, in many cases this is hardly surprising since some data used to construct Figures 1 and 3 were also used to construct Figure 4. Nevertheless, sufficient experimental data and independent estimates were used to make the HO orbital energies quite reliable, and the relative LU orbital energies only somewhat less so.

These estimates have been made for the parent systems, but not all the parents are known even as reactive intermediates. All of the parent diazonium betaines, as well as formonitrile oxide, ozone, methylene nitrone, and formaldehyde oxide, are known as isolable compounds or reactive intermediates, but the majority of cycloaddition studies have involved substituted dipoles. Calculations on some of the substituted systems have been carried out, and qualitative generalizations can be made about the effect of substituents on 1,3-dipole frontier orbital energies and coefficients. Before doing this, a discussion of substituent effects on alkene frontier orbital energies and coefficients will be given, since much more experimental data are available from which to make reliable estimates.

Dipolarophile Frontier Orbitals. We shall group substituted ethylenes into three broad classes, electron-rich (CH_2CHX), electron-deficient (CH_2CHZ), and conjugated (CH_2CHC), and derive qualitative conclusions about frontier orbital energies and coefficients.[54a]

Ethylene. The ionization potential of ethylene is

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(52) K. N. Houk, unpublished results.

(53) J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc. C*, 1073 (1969).

(54) T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Jap.*, **36**, 1552 (1963); T. Kubota and M. Yamakawa, *ibid.*, **36**, 1564 (1963).

(54a) NOTE ADDED IN PROOF. A similar treatment of alkene frontier molecular orbitals has appeared: N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 5625 (1973). We thank Professor Epiotis for a preprint of this manuscript.

Table V. π Ionization Potentials and Electron Affinities of Some Dipolarophiles

Dipolarophiles	*IP*, eV	*EA*, eV
Parent		
Ethylene	10.51^a	$-0.84,^b$ 1.69^k
Acetylene	11.40^a	
Electron-Rich		
Alkyl (–R)		
Propene	9.73^d	-0.9^c
1-Octene	9.43^e	
2-Butene	9.13^d	
3-Ethyl-2-pentene	8.53^f	
Norbornene	8.97^g	
$-\ddot{X}$		
1-Pyrrolidinocyclopentene	7.33^h	
1-Morpholinocyclopentene	8.80^h	
n-Butyl vinyl ether	9.08^h	-0.7^c
Methyl vinyl ether	8.93^d (IP_{ad})	
Vinyl acetate	10.76^u	
Vinyl fluoride	10.31^a	
Vinyl chloride	10.00^d (IP_{ad})	
Vinyl bromide	9.80^d (IP_{ad})	
Conjugated (–C)		
Butadiene	9.08^a	-0.32^j
Styrene	$8.48,^{i,v}$ 10.47	-0.55^j
Vinylcyclopropane	9.2^k	
Phenylacetylene	$8.82\ (\pi_z)^i$ $10.36\ (\pi_y)^i$	-1.25^j
Electron-Deficient		
–Z		
Methyl acrylate	10.72^l	0.8^c
Ethyl acrylate		$0.2_5{}^m$
Methyl crotonate	10.11^l	
Acrylonitrile	10.91^h	1.2^m
Acrolein	$10.93,^a$ 11.07^l	1.3^c
Methacrolein	10.60^m	1.3^c
Propynal		0.7^c
Cyanoacetylene	11.81^a	
Methyl propiolate	11.15^h	
$(-Z)_n$		
Dimethyl maleate	11.0^l	0.6^m
Fumaronitrile	11.15^p	$0.78,^p$ -0.04^q
Tetracyanoethylene		$1.80,^l$ $2.89,^m$ 1.80^p
Maleic anhydride		$1.80,^m$ 2.89^o
Dibenzoylethylene		0.25^r
Conjugated Dienes		
Butadiene	9.08^a	
1-Substituted		
trans-Piperylene	8.78^r	
1-Phenylbutadiene	8.16^r	
1-Methoxybutadiene	8.21^r	
Anthracene	7.59^s	$0.57,^t$ 0.61^j
trans-Hexatriene		0.17^j
2-Substituted		
Isoprene	9.04^q	
2-Phenylbutadiene	8.77^q	
2-Methoxybutadiene	8.62^q	

[a] Reference 27. [b] Reference 49. [c] Estimated here from substituent effects on reduction potentials given in ref 59. [d] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1972); see also L. S. Levitt, B. W. Levitt, and C. Párkányi, *Tetrahedron*, **28**, 3369 (1972). [e] D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970). [f] D. A. Demeo and A. J. Yencha, *ibid.*, **53**, 4356 (1970). [g] P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969). [h] R. Sustmann, unpublished results cited in R. Sustmann and H. Trill, *Angew. Chem. Int. Ed. Engl.*, **11**, 838 (1972). [i] J. W. Rabalais and R. J. Cotton, *J. Electron Spectrosc.*, **1**, 83 (1972/73). [j] Calculated in ref 29. [k] R. Gleiter, E. Heilbronner, and A. de Meijere, *Helv. Chim Acta*, **54**, 1029 (1971). [l] Reference 69. [m] Reference 54. [n] Estimated from ref 62; see text. [o] Reference 62. [p] H. Bock and H. Stafast, *Chem. Ber.*, **105**, 1158 (1972). [q] A. I. Konovalov, V. D. Kiselev, and O. A. Vigdorovich, *J. Org. Chem. USSR*, **3**, 2034 (1967). [r] Reference 63. [s] Reference 61. [t] L. E. Lyons, G. C. Morris, and L. J. Warren, *Aust. J. Chem.*, **21**, 853 (1968). [u] Reference 52. [v] Mainly phenyl.

10.51 eV.[27e] The electron affinity of ethylene has been estimated as −0.84 eV from spectroscopic data.[55] This value seems high since the electron affinity of benzene is about −1.5 eV. *Ab initio* calculations give electron affinities ranging from −1.7 to −6.7 eV,[56] while a measurement of the "adiabatic" electron affinity gives $EA \geq 0.9$ eV.[57] We have chosen the value of −1.5 eV as a realistic value. This value for *EA*, the *IP* of 10.5 eV,[27] and the $\pi\pi^*$ energy of 7.7 eV[58] give a calculated Δ of 4.3 eV for ethylene.

The orbital energies of substituted ethylenes are fixed with respect to these values and shown in Figure 7. The orbital energies in this figure are based on experimental values of π ionization potentials for compounds of a given class and on measured or estimated electron affinities. Table V collects representative data from which these numbers are derived.

Electron-Rich Alkenes. Two major subclasses of these compounds may be considered. The alkyl ethylenes generally have ionization potentials 1–2 eV lower than ethylene, depending on the type and number of alkyl substituents. The $\pi\pi^*$ transition energies of alkyl ethylenes are 0.6–1.0 eV lower in energy than that of ethylene.[58] The value of $IP - E_{\pi\pi^*}$ decreases regularly from 2.93 eV for ethylene to 1.69 eV for tetraalkylethylenes, whereas the *IP* decreases from 10.51 to 8.20 eV. This indicates either that the LU increases in energy more slowly than the HO with alkyl substitution or that Δ increases regularly along the series. The former effect is assumed to predominate here. This is a reasonable assumption since the HO is raised inductively and by mixing with lower-lying alkyl σ orbitals, while the LU is raised by inductive effects and lowered by mixing with higher energy σ* orbitals.

The second type of electron-rich alkenes is substituted with more powerful donors such as alkoxy or amino groups. The trends in destabilization are similar, but more drastic for this type of substitution than for alkyl substitution.

Conjugated Alkenes. Conjugating substituents raise the HO and lower the LU orbital energies of ethylene. The electron affinities of conjugated alkenes can be indirectly estimated in the following ways. House and coworkers found that a 1- or 3-phenyl substituent changed the reduction potential of acroleins by about 0.4 V.[59] The change in electron affinity from that of ethylene can thus be assumed to be 0.4–0.8 eV. A comparison of reduction potentials of some electron-deficient and conjugated alkenes shows that the latter are about 0.5 V more difficult to reduce than the former.[59b] A third estimate results from comparison of $\pi\pi^*$ transition energies of ethylene (7.7 eV) and butadiene (5.7 eV).[60] Assuming a constant Δ and noting the difference in ethylene and butadiene *IP*'s of 1.4 eV, the *EA* of butadiene is estimated to be 0.6 eV lower than that of ethylene. Calculated electron affinities for styrene are in general accord with these estimates.[61]

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(55) K. Kimura and S. Nagakura, *Theor. Chim. Acta*, 3, 164 (1965).

(56) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, 48, 191 (1968).

(57) R. N. Compton, R. H. Huebner, P. W. Reinhardt, and L. G. Christophorou, *J. Chem. Phys.*, 48, 901 (1968).

(58) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(59) (a) H. O. House, L. E. Huber, and M. J. Umen, *J. Amer. Chem. Soc.*, 94, 8471 (1972); (b) D. A. Tyssee, J. H. Wagenknecht, M. M. Baizer, and J. L. Chruma, *Tetrahedron Lett.*, 4809 (1972).

(60) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 58.

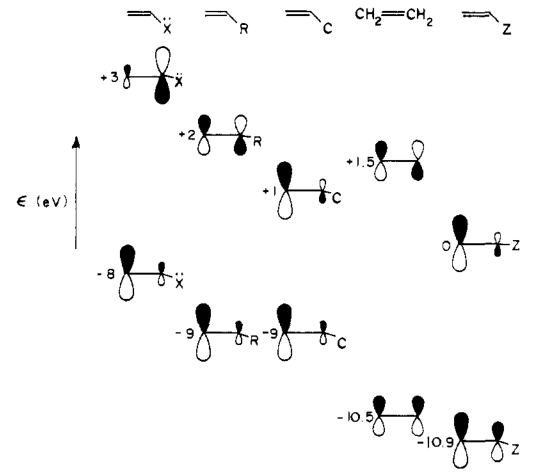

Figure 7. Estimated π frontier orbital energies and coefficients for dipolarophiles.

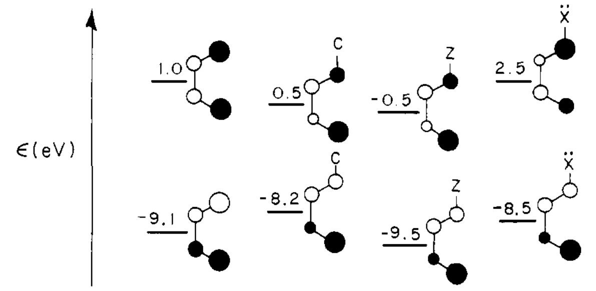

Figure 8. Estimated frontier orbital energies and coefficients for 1-substituted butadienes.

Electron-Deficient Alkenes. A single electron-withdrawing substituent which is simultaneously conjugating (–COR, –CN, etc.) lowers the HO energy of ethylene only slightly but has a much larger effect on the LU energy. For these compounds, both ionization potentials and electron affinity data are available and are shown in Table V. The estimated values for acrylonitrile come from the observation that each cyano group raises the electron affinity of polycyanoethylenes by 0.55 eV.[62] Carbonyl group attachments raise aromatic *EA*'s by 1.5–2 eV.[32] Figure 7 assumes a conservative value for the *EA* of mono-*Z*-alkenes. Two electron-withdrawing groups will, of course, further raise both the *IP* and the *EA*. The reduction potential of maleate is about 0.6 V more positive than that of acrylate.[59b]

Butadienes. Table V also shows limited available data on substituted butadienes. Measured substituent effects on butadiene frontier orbital energies are similar to those on ethylene frontier orbital energies, and Figures 8 and 9 are constructed assuming this parallel. As predicted from perturbation theory (see below) and observed in the photoelectron spectra of butadienes,[63] substituent effects on frontier orbital energies will decrease as the MO coefficient at the site of attachment decreases. That is, substituent effects on both HO and LU energies fall in the order ethylene > 1-butadiene > 2-butadiene.

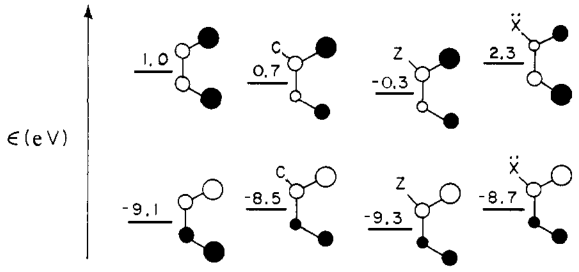

Figure 9. Estimated frontier orbital energies and coefficients for 2-substituted butadienes.

Coefficients. The generalized coefficient magnitudes in Figures 7–9 are derived mainly from CNDO/2 and EH calculations performed here, or from calculations available in the literature.[63a] Since all of the available calculations agree on the relative magnitudes of frontier orbital coefficients except in the case of electron-deficient dipolarophile HO orbitals, details of these calculations will not be reproduced here except where disagreements among calculations arise.

Electron-Rich Alkenes. The shapes of the frontier orbitals can be qualitatively derived from first-order perturbation theory.[16,17,64] Assuming that substituents exert a purely inductive effect on the ethylenic carbon to which they are attached, electron-releasing groups will lower the coefficient at the point of attachment in the HO and raise that coefficient in the LU. Calculations performed here and in the literature invariably show this behavior for alkyl, amino, alkoxy, and halo substituents.[20,21,65] The same relative coefficient magnitudes also result from "hyperconjugation" models or pseudo-π models for alkyl substituents.[66] In such models, the HO resembles a perturbed allyl Ψ_2, and the LU resembles a perturbed allyl Ψ_3.

Conjugated Alkenes. The union of two π systems results in a decrease in the coefficient at the site of union in both the HO and LU. Numerous calculations confirm the similarity of the frontier orbitals shown in Figure 7 to those calculated by simple Hückel methods.[20,63–66]

Electron-Deficient Alkenes. An inductive model of electron-deficient alkenes predicts that the larger terminal coefficient is on the substituted carbon in the HO and the unsubstituted carbon in the LU. This arises from mixing of two 2p orbitals of unequal energy, for which the carbonyl group π orbitals provide a familiar model. These orbitals would resemble Ψ_1 and Ψ_2 of the allyl system, respectively. Such a pattern is expected for substituents such as trifluoromethyl or carbonyl groups which are twisted out of conjugation with an alkene, or in the in-plane occupied π orbital of methyl propiolate. However, most common electron-withdrawing groups are also conjugating, and the latter effect tends to diminish the coefficient at the site of

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(61) R. P. Blaunstein and L. G. Christophorou, *Radiat. Res. Rev.*, **3**, 69 (1971).

(62) A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **63**, 2369 (1967).

(63) R. Sustmann and R. Schubert, *Tetrahedron Lett.*, 2739 (1972).

(63a) NOTE ADDED IN PROOF. The absolute values of the HO and LU coefficients of a substituted alkene are smaller, and may be much smaller, than those of ethylene.

(64) W. C. Herndon, *ibid.*, 125 (1971); W. C. Herndon, *Fortschr. Chem. Forsch.*, in press.

(65) For example, see W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 6529 (1972).

(66) C. A. Coulson and A. Streitweiser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965; A. Streitweiser, Jr., and J. I. Brauman, "Supplementary Tables of Molecular Orbital Calculations," W. H. Freeman, San Francisco, Calif., 1965.

attachment in the HO and the LU. The competition and cooperation of these two effects in the HO and LU orbitals, respectively, can clearly be seen in the relatively slight lowering of the ethylene HO and large lowering of the LU of ethylene by electron-withdrawing groups.

All methods of calculation predict the same relative magnitude for the LU's of these compounds, as shown in Figure 7. CNDO/2 (this work and ref 20), INDO,[67] and *ab initio*[68] calculations predict that for molecules of this type (*e.g.*, acrolein), the alkene coefficient at the unsubstituted carbon in the HO should be larger, while Hückel,[64] EH (this work), and MINDO/2[21] predict the opposite relative coefficient magnitudes.[12] Photoelectron spectroscopy can be used to provide evidence for the former relative ordering of coefficient magnitudes. The change of HO energy should be roughly proportional to the square of the coefficient at the site of attachment. The decrease in lowest ionization potential upon β-methylation of acrolein or methyl acrylate is 1.68 and 1.39 times, respectively, that upon α-methylation.[69] Similarly, β-methylation of acrylonitrile raises the HO 1.25 times more than α-methylation.[52]

Dienes. The same types of coefficient changes that occur for alkenes lead to Figures 8 and 9 for the substituted butadienes. Calculations are again in some doubt as to the HO coefficients of electron-deficient dienes.[70]

Polysubstituted Alkenes. We have carried out calculations by the CNDO/2 method on a large number of disubstituted alkenes. The numerical results are mercifully omitted here, since they are in accord with qualitative reasoning. Results in the literature confirm this conclusion.[20] To summarize, the effect of two substituents on frontier orbital coefficients is roughly the sum of the individual effects of the two substituents. For example, α-methylacrylonitrile has the larger HO coefficient on the unsubstituted carbon (both substituents reinforce this) and approximately identical coefficients at both carbons in the LU (the two substituents have opposite effects). For a cinnamic ester, the larger HO coefficient is on the carbon attached to the ester (phenyl has a larger effect on HO coefficients than an ester), but the LU coefficients are about the same (the two substituents have opposite effects of nearly the same magnitude).

These qualitative considerations may be summarized as follows (*cf.* Figure 7): (1) conjugating substituents destabilize the ethylene HO orbital to a greater extent than they stabilize the LU orbital; (2) electron-withdrawing substituents stabilize the ethylene LU more than they stabilize the HO orbital; and (3) electron-releasing substituents destabilize the ethylene HO orbital more than they destabilize the LU orbital. These conclusions are not entirely consonant with those reported earlier based on first-order perturbation arguments.[64] However, the gross conclusions are the same in both treatments.

Acetylenic Dipolarophiles. Although the general characteristics of alkenes and alkynes are similar, some rather important qualitative differences between these species are known. Acetylenes are known to undergo reactions with electrophiles considerably less readily that do the corresponding ethylenes. Conversely, reactions of nucleophiles with acetylenes are faster than those with the corresponding ethylenes. Although first-order (Coulombic) effects are undoubtedly of some importance, these chemical observations suggest that both the HO and LU orbitals of an acetylene are lower in energy than those of the corresponding alkenes. The lower HO energy is amply confirmed by photoelectron spectroscopy. Table IV shows some selected values of the *IP*'s of acetylenic dipolarophiles. In general, the HO orbital energy of an acetylene is 0.4 to 0.9 eV lower than that of the corresponding alkene.

Calculations predict that the HO should be lower but the LU higher for acetylenes than for alkenes. Qualitatively, this results from a decrease in the CC bond length and concomitant larger overlap of the p orbitals, resulting in more bonding in the HO and more antibonding in the LU. Qualitatively, these two energy changes should be the same. Computationally, the HO of acetylene is invariably lower than that of ethylene in CNDO/2 and EH calculations (this work) and in *ab initio* calculations.[71–73] Calculations of this type give the first virtual orbital of acetylene at higher energy than that of ethylene.[72,73] However, the destabilization of the LU π^* orbital is calculated to be 0.3–0.7 that of the stabilization of HO π orbital.[73] Similar comparisons on the *ab initio* level are available for propene and propyne.[74] Experimental evidence for the LU orbital energies comes from the reduction potentials of α,β-acetylenic carbonyl compounds, which are only 0.1 V less negative than those of the corresponding α,β-olefinic carbonyl compounds,[59a] and from the $\pi\pi^*$ transition of phenylacetylene (5.17 eV), which is quite similar to that of styrene (5.01 eV).

Thus it appears that the LU energies of electron-deficient acetylenes do not differ much from those of the corresponding electron-deficient alkenes. A further point of importance is the fact that one of the acetylene π or π^* orbitals will be affected by conjugation and the other only by electronegativity effects.

Substituent Effects on 1,3-Dipole Frontier Orbital Energies. Since little experimental data are available as yet to determine the effect of dipole substituents on frontier orbital energies and coefficients, only a brief and very qualitative discussion will be attempted. We assume, first, that the effect of various types of substituents on dipole frontier orbital energies and coefficients will be qualitatively similar to the effect of these substituents on dipolarophile frontier orbital energies and coefficients. Experimental or computational evidence will be cited also where available.

Assuming the simple perturbation model for substituent effects used earlier, the effect of a substituent on dipole energies is expected to be a function of the magnitude of the coefficient at the site of attachment. Thus, for the dipole HO's, substituent effects should be

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(67) R. R. Birge and P. A. Leermakers, *J. Amer. Chem. Soc.*, 94, 8105 (1972).

(68) A. Devaquet, *ibid.*, 94, 5160 (1972).

(69) R. Sustmann and H. Trill, *Tetrahedron Lett.*, 4271 (1972).

(70) T. Fueno and K. Yamaguchi, *J. Amer. Chem. Soc.*, 94, 1119 (1972).

(71) J. W. Moskowitz, *J. Chem. Phys.*, 43, 60 (1965); 45, 2338 (1966).

(72) W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 2384 (1966).

(73) R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *J. Chem. Phys.*, 46, 2029 (1967).

(74) M. D. Newton and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 89, 4261 (1967); M. L. Unland, J. R. Van Wazer, and J. H. Letcher, *ibid.*, 91, 1045 (1969).

in the order "anionic" terminus > "neutral" terminus ≫ central atom, for position of substituent attachment. For the LU, the corresponding order anticipated is "neutral" terminus ~ central atom > "anionic" terminus. Of course, only the azomethinium betaines can have a substituent on the central atom.

Electron-Releasing Substituents. A comparison of the formonitrile oxide and acetonitrile oxide calculations shows the HO raised by 0.9 eV and the LU lowered by 0.1 eV by alkyl substitution. The coefficients at both termini are decreased to about the same extent.

We have also carried out calculations on *N*-methylmethylenenitrone which indicate a 0.5 eV raising of the parent HO and a 0.2 eV raising of the parent LU by N-methylation. Essentially identical changes are found on comparison of *C*-phenylnitrone and *C*-phenyl-*N*-methylnitrone calculations. The relative magnitude of the carbon coefficient increases in the HO and decreases in the LU upon N-methylation; these results are parallel to those found for alkenes, assuming the immonium linkage resembles an alkene.

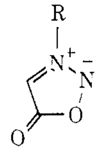
Experimental verifications of these conclusions are not readily available, although some indirect evidence is available in the literature. The $\pi\sigma^*$ and $\pi\pi^*$ transitions of *n*-butyl azide are red-shifted 0.39 and 0.06 eV, respectively, compared to those of hydrazoic acid,[43] which can be construed as evidence for greater destabilization of the HO than the LU orbital. A more extensive tabulation of azide transition energies reveals the expected trends; that is, increasingly good inductive donor alkyl groups lower the transition energies to a greater extent.[44] Until ionization potentials of a large series of 1,3 dipoles have been measured, no quantitative measure of the effect of substituents on dipole energies can be made. However, it is notable that CNDO/2 calculations predict a 1.7 eV decrease in *IP* upon methylation of ethylene (*vs.* 0.8 eV experimentally) while methylation of formonitrile oxide leads to a calculated lowering of 0.9 eV. This ratio of calculated ΔIP's is 1.9, while the ratio of $(C_{\mathrm{HO}})^2$ at site of attachment is 1.7. If the experimental trends are similar, then the HO of acetonitrile oxide should be raised by about 0.4 eV above that in formonitrile oxide. As a crude rule of thumb based on coefficient magnitudes of dipoles *vs.* those in alkenes, alkyl substitution should have about half the effect on orbital energies in dipoles as in alkenes. The effects of better donors ($-\ddot{X}$) on dipole orbital energies are also assumed to parallel the effects on alkenes.

Conjugating Substituents. Using arguments like those in the preceding section, conjugation should compress the frontier orbital energies. CNDO/2 calculations on arylnitrile oxides, *C*-phenylnitrones, and vinyldiazomethane confirm this. Conjugating substituents decrease the coefficient at the site of attachment in alkenes, and calculations confirm this trend for nitrones and the benzonitrile oxide LU but not in benzonitrile oxide HO, where the relative magnitude of HO coefficients does not change appreciably. Given the usual order of coefficient magnitudes in dipoles, attachment of an aryl group at the "neutral" terminus should decrease the difference in terminal coefficients in the LU and have a smaller effect on this difference in the HO. Attachment at the "anionic" terminus should have the opposite effect in the LU.

Photoelectron spectra of *N*-*tert*-butylmethylenenitrone and *C*-phenyl *N*-methyl nitrone that we have measured give an estimate of the magnitude of energy changes induced by phenyl substitution or alkyl substitution in a 1,3 dipole.[52] The π ionization potential of *N*-*tert*-butylmethylene nitrone is assigned to the 8.64 eV band. Since a *tert*-butyl group lowers the ionization potential of an alkene by about 0.3 eV as compared to a methyl, we can estimate the π ionization potential of *N*-methylmethylene nitrone as about 9 eV. The measured ionization potential of *C*-phenyl-*N*-methylnitrone at 7.89 eV indicates a 1.1 eV raising of the nitrone HO by phenyl. This is to be compared with the roughly 1.5–2.0 eV raising of the HO of ethylene by conjugating substituents (Table IV).

The $\pi\pi^*$ transitions of *N*-*tert*-butylnitrone and *C*-phenyl-*N*-methylnitrone at 5.16[53] and 4.23 eV[54] represent a bathochromic shift of 0.93 eV, most of which can be accounted for by the 0.75 eV difference in HO energies. Thus, as with alkenes, the lowering of the dipole LU by conjugation is smaller than the raising of the HO.

Electron-Withdrawing Groups. Extensive calculations on such systems have not been performed, but our previous discussion would indicate a similarity between substituent effects on dipoles and alkenes. The sydnones, shown below, are one well known class of substituted azomethine imines.



Calculations performed here by EH and CNDO/2, as well as published HMO,[75] ω-HMO,[76] PPP,[77] and CNDO/2 and INDO[78] calculations, indicate a pronounced lowering of the LU orbital and a lesser lowering of the HO. The "electron-withdrawing end" of the carboxyl group, which will cause lowering, is attached to the position of large coefficient in the LU, small in the HO, while the weakly "electron-releasing end" of the carboxyl has a greater effect on the HO than the LU. Calculations indicate that the terminal coefficients of the azomethine imine system are almost identical in the LU. This agrees well with the aforementioned qualitative approach to coefficient charges. That is, the CO attachment will lower the LU coefficient at the site of attachment, while the O attachment will raise the LU coefficient at the site of attachment. Both tend to level or reverse the normal larger magnitude of the C coefficient in the LU.

Qualitative Estimations of Substituent Effects. Using the first-order perturbation approximation for substituent effects, a substituent effect on a dipole energy can be estimated as $\Delta E_{\mathrm{d}} = C_{\mathrm{d}}^2/C_{\mathrm{e}}^2(\Delta E_{\mathrm{e}})$, where ΔE_{d} is the change in dipole frontier orbital energy, C_{d} is the dipole coefficient at the site of substitution (from

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[75] J. A. Singer and W. P. Purcell, *J. Med. Chem.*, 10, 754 (1967).

[76] E. B. Roche and L. B. Kier, *Tetrahedron*, 24, 1673 (1968).

[77] K. Sundaram and W. P. Purcell, *Int. J. Quantum Chem.*, 11, 145 (1968).

[78] R. A. Coburn and J. D. O'Donnell, *J. Org. Chem.*, 37, 1707 (1972).

Table III), C_e is the ethylene coefficient ($1/\sqrt{2}$), and ΔE_e is the change in frontier orbital energy of ethylene caused by substitution (Figure 7).

Summary. We have derived, wherever possible from experimental data, a set of rules for the qualitative deduction of the coefficients and energies of all common 1,3 dipoles, dienes, and dipolarophiles. These last compounds are, of course, also dienophiles, enophiles, ketenophiles, sulfenophiles, etc., so that these considerations should lead not only to increased understanding of 1,3-dipolar cycloadditons[12,13] but also to an understanding of all types of cycloaddition reactions.

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The Origin of Reactivity, Regioselectivity, and Periselectivity in 1,3-Dipolar Cycloadditions

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Abstract: Perturbation theory is applied to 1,3-dipolar cycloaddition phenomena. The generalizations made in the previous paper concerning 1,3 dipole and dipolarophile frontier orbital energies and coefficients allow a specific qualitative treatment of reactivity of individual 1,3 dipoles. The explanation of regioselectivity and periselectivity phenomena also follows from this treatment. Extensions of the frontier orbital method to other cycloaddition reactions are outlined.

The previous paper derived a set of generalized frontier orbitals of 1,3 dipoles and dipolarophiles.[4] The motive of that exercise was to develop a simple, yet theoretically meaningful, explanation of perplexing regioselectivity phenomena observed in 1,3-dipolar cycloadditions. The use of these generalized frontier orbitals within the framework of qualitative perturbation molecular orbital theory will be shown here to provide a qualitative explanation for the phenomena of differential reactivity, regioselectivity, and periselectivity in 1,3-dipolar cycloadditions as well as provide additional insight into selectivity phenomena observed in Diels–Alder reactions and thermal and photochemical [2 + 2] cycloadditions.

Applications of Perturbation Theory to Cycloadditions. Perturbation theory has been an increasingly powerful tool for the understanding of diverse organic phenomena.[5,6] Applications of perturbation theory to cycloaddition reactions have recently been reviewed.[7] Salem has derived the following second-order perturbation expression for the change of energy which accompanies the interaction of two molecules involved in a cycloaddition reaction.[7,8]

$$\Delta E = -\sum_{ab}(q_a + q_b)\gamma_{ab}S_{ab} - \sum_{ab} Q_a Q_b \frac{\Omega}{\epsilon} + 2\sum_{R}^{\text{occ}}\sum_{S}^{\text{unocc}} - \sum_{R}^{\text{unocc}}\sum_{S}^{\text{occ}} \frac{\left(\sum_{rs} c_a c_b \gamma_{ab}\right)^2}{E_R - E_S} \quad (1)$$

The first term is a closed-shell repulsion term, the second term is a Coulombic repulsion (or attraction) term, and the third term is called variously the delocalization, overlap, or charge-transfer stabilization. In this equation q_a's and Q_a's are orbital and total electron densities, respectively, at atomic orbital a in molecular orbital R, γ_{ab} is the interorbital interaction integral and S_{ab} is the interorbital overlap integral for atomic orbitals a and b in MO's R and S, and c_a's are the atomic orbital coefficients at atom a in molecular orbital R. The last term is a quantitative expression of the qualitative statement that interaction of two orbitals results in depression of the energy of the lower energy orbital and raising of the energy of the higher energy orbital, with the extent of energy change inversely proportional to the difference in energy of the orbitals prior to interaction.[5] This is shown schematically in Figure 1 for the interaction of the HO (E_1) of one polyolefin with the LU (E_2) of a second.

Most perturbation treatments of cycloaddition reactivity have focused on the last term of eq 1 and have

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(4) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Amer. Chem. Soc.*, **95**, 7287 (1973).

(5) E. Heilbronner and H. Bock, "Das HMO-Modell und Seine Anwendung," Verlag-Chemie, GmbH, Weinheim/Bergstr., 1968; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971); R. F. Hudson and G. Klopman, *Tetrahedron Lett.*, 1103 (1967); G. Klopman, *J. Amer. Chem. Soc.*, 90, 223 (1968).

(6) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970); *Accounts Chem. Res.*, 4, 57 (1971).

(7) W. C. Herndon, *Chem. Rev.*, 72, 157 (1972).

(8) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

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