it is not possible to obtain a very high quantitative accuracy. The intention of the present work is to get qualitatively correct results, and energy differences of a few kilocalories should not be interpreted as significant differences. The most severe limitation of the calculations when the results are compared with experimental observations is, of course, the model systems used, the fact that there are no extra ligands on nickel, that there is no solution around the complex, and so on. But within the present model the most severe restriction is probably the quality of the basis set. Test calculations did, however, show that neither f functions on nickel nor d functions on carbon change the results qualitatively. The main effect of f functions on nickel is to give a better energy splitting of the atomic states, and since the d population on nickel is fairly constant along the potential surface, the f functions are not expected to influence the shape of the surface very much. d functions on carbon decreased the binding energy of $Ni(CH_3)_2$ by 4 kcal/mol, from −5 to −9 kcal/mol.

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Registry No. $Ni(CH_3)_2$, 54836-89-4; $Ni(H)CH_3$, 86392-32-7; Ni, 7440-02-0; ethane, 74-84-0; methane, 74-82-8.

Ionization Potentials, Electron Affinities, and Molecular Orbitals of 2-Substituted Norbornadienes. Theory of 1,2 and Homo-1,4 Carbene Cycloaddition Selectivities

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Abstract: The ionization potentials, electron affinities, and π orbital shapes of 2-substituted norbornadienes have been determined by photoelectron spectroscopy, electron-transmission spectroscopy, and ab initio molecular orbital calculations, respectively. The deductions made about the electronic structures of 2-methoxy-, (trimethylsiloxy)-, chloro-, cyano-, (methoxycarbonyl)-, and phenylnorbornadienes permit a detailed interpretation of the reactivities and selectivities observed experimentally in carbene cycloadditions to these molecules. A substituent at C-2 of norbornadiene not only affects the 2–3 π bond but also influences the 5–6 π bond due to through-space interactions between π orbitals. The orbital energy changes and polarization induced by 2-substituents provide a compelling rationale of the variations in 1,2 and homo-1,4 cycloadditions of carbenes to these species, and confirm the electrophilic nature of both of these cycloadditions.

Can anything more be discovered about subtle electronic effects in norbornadiene? This molecule and derivatives thereof have been subjected to virtually every type of chemical abuse imaginable, yet new phenomena continue to pour forth from experimental and theoretical studies of this battered framework. Apart from the monumental accumulation of data on the solvolysis of norbornyl derivatives, the amount of information about electrophilic,[2] nucleophilic,[3] and radical reactions[4] on norbornenes and norbornadienes is substantial. Our own interests in norbornadienes have been in the study of Diels–Alder,[5] carbene,[6,7] and singlet-oxygen[8] reactions of these molecules, as well as our studies of the molecular deformations of the alkene moieties caused by the basic ring skeleton together with its substituents.[9]

Table I. Adducts Obtained from the Addition of Difluorocarbene to 2-Substituted Norbornadienes[a]

reactant 2-R-norbornadiene R =	exo-1,2 adducts		endo-homo-1,4 adducts		exo-1,2/ homo-1,4 ratio
	syn	anti	anti	syn	
–OMe	89.0		11.0		8.1
$-OSiMe_3$	75.0	6.0	6.0		4.2[b]
–Ph	75.0		25.0		3.0
–Cl	62.0	4.0	34.0		1.9
–H	33.0	33.0	34.0		1.9
$-CO_2Et$	44.0	12.0	44.0		1.3
$-CO_2Me$	38.0	15.0	47.0		1.1
–CN	35.0	23.0	30.0	12.0	1.4

[a] Yields are normalized to 100%. [b] Three other products are formed (13%), but have eluded characterization so far. One of these may be the 1,4 adduct.

Our new obsession with 2-substituted norbornadienes arose from the discovery in the Geneva laboratories of the exo-1,2, endo-1,2, and endo-homo-1,4-cycloadditions defined in Figure 1. In 2-

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(2) Freeman, F. *Chem. Rev.* **1975**, *75*, 439. See, for example, Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *J. Am. Chem. Soc.* **1973**, *95*, 2209 and references therein.

(3) See, for example: Richey, H. G., Jr.; Wilkins, C. W., Jr. *J. Org. Chem.* **1980**, *45*, 5027. Richey, H. G., Jr.; Wilkins, C. W., Jr.; Bension, R. M. *J. Org. Chem.* **1980**, *45*, 5042.

(4) See, for example: Davies, D. I.; Parrot, M. J. *Tetrahedron* Lett. **1972**, 2719.

(5) Mazzochi, P.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482.

(6) Jefford, C. W.; Kabengele, nT.; Kovacs, J.; Burger, U. *Helv. Chim. Acta* **1974**, *57*, 104; *Tetrahedron Lett.* **1974**, 257; Kwantes, P. M.; Klumpp, G. W. *Ibid.* **1976**, *707*. Jefford, C. W.; Mareda, J.; Gehret, J. C. E.; Kabengele, nT.; Graham, W. D.; Burger, U. *J. Am. Chem. Soc.* **1976**, *98*, 2585.

(7) Jefford, C. W.; Phan Thanh, Huy *Tetrahedron Lett.* **1980**, 755.

(8) Jefford, C. W.; Rimbault, C. G. *J. Org. Chem.* **1978**, *43*, 1908; *J. Am. Chem. Soc.* **1978**, *100*, 295, 6437, 6515; *Tetrahedron Lett.*, **1979**, 985.

(9) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.*, **1981**, *103*, 2438.

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Table II. Vertical Ionization Potentials (eV) and Electron Affinities (eV) of 2-Substituted Norbornadienes and Norbornenes

	IP's				EA's	
	π	π_-	π_+	other	π_+^*	π_-^*
norbornadiene		8.69	9.55		−1.04	−2.56
2-methoxynorbornadiene		8.05	9.27		−1.35	−2.85
2-(trimethylsiloxy)-norbornadiene		8.06	9.07		−1.15	−2.77
2-chloronorbornadiene		8.77	9.68	11.27 (σ) 11.68 (n_{Cl})	−0.83	−2.06
2-cyanonorbornadiene		9.26	10.12	11.41 (σ) 11.68 (n_{CN})		
2-(methoxycarbonyl)-norbornadiene		8.92	9.72	10.26 (n_{CO}) 10.9 (n_O)		
2-phenylnorbornadiene		9.06	9.92	7.97 (Ph_S) 9.06 (Ph_A)		
norbornene	8.97					
2-methoxynorbornene	8.15					
2-(trimethylsiloxy)-norbornene	8.09					

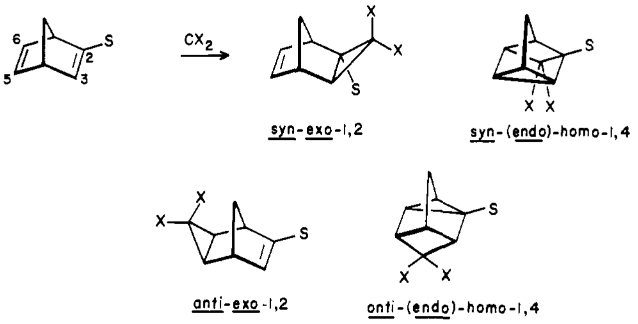

Figure 1. Nomenclature of carbene cycloadditions to 2-substituted norbornadienes.

substituted norbornadienes, there are two regioisomerically distinct versions of each of these reactions, which we call syn and anti. We have reported how the substituent, S, exerts profound effects upon product ratios.[7] The results are summarized in Table I. Several interesting trends are revealed in this table. First, the preference for 1,2 over homo-1,4 cycloaddition is maximum for electron-donating substituents (8.1:1 for MeO), and essentially disappears with good electron-withdrawing substituents (1.1:1 for CO_2Me). Second, the syn-1,2:anti-1,2 ratio drops regularly from greater than 20:1 with MeO (only syn is observed, but a few percent of the anti could have escaped detection) to 1.5:1 for CN. Third, anti-homo-1,4 cycloaddition is preferred over syn. Only the cyano compound gives an observable syn-homo-1,4 adduct. It is difficult to interpret these trends in terms of simple ideas about substituent effects, since it is not possible to determine, without more detailed investigations, the relative effect of substituents on the attached alkene and the remote alkene. The two alkene π bonds are known to interact extensively, so that substitution of one should influence the other to some extent. Fujimoto has provided a perturbation model to treat such homoconjugated systems, and has rationalized orientation effects in electrophilic additions to substituted homoconjugated species.[10]

In this paper, we present a detailed investigation of the electronic structures of norbornadienes substituted at the 2-position by various electron-donating, conjugating, and electron-withdrawing substituents. The techniques used are photoelectron spectroscopy, electron-transmission spectroscopy, and ab initio molecular orbital calculations. The spectroscopic and computational results will be described first, and then a comprehensive model to explain the data in Table I will be developed.

Ionization Potentials. The photoelectron spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer with use of a He (I) source, with argon and xenon as internal calibrants. The resolution for each determination is approximately 25 meV. Each vertical ionization potential (IP) reported corresponds to the average peak height, obtained from at least five determinations. Because of the relative sharpness of the bands, the values given are expected to be accurate to within ±0.04 eV. Since the spectra are very similar in appearance to that of norbornadiene,[11] they are not reproduced here. The vertical ionization potentials of six 2-substituted norbornadienes and two 2-substituted norbornenes are given in Table II, together with those of norbornadiene and norbornene. The assignments of the IP's were derived in straightforward correlative manner, as shown in Figure 2.

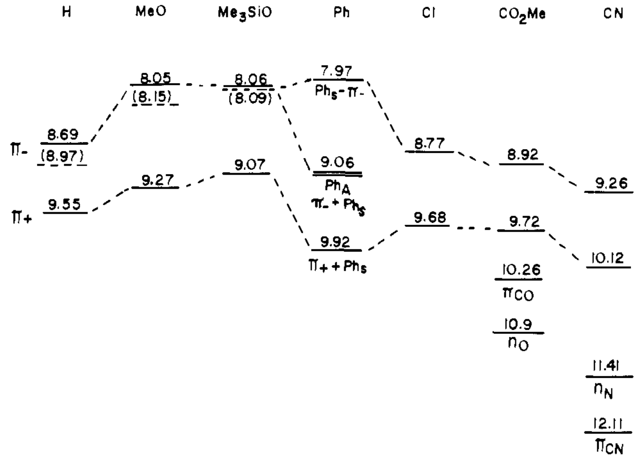

Figure 2. Correlations between the π ionization potentials of norbornadiene and 2-substituted norbornadienes. Dashed lines are π IP's of the corresponding norbornenes.

The first IP of norbornene is 8.97 eV and arises from ionization from the π orbital.[11] In norbornadiene, there are two π orbitals and two corresponding IP's; the first at 8.69 eV results from the through-space antibonding combination of the π orbitals (π_-) and the second at 9.55 eV is due to the bonding combination (π_+).[11] These orbitals, and the corresponding vacant π^* orbitals, are shown in Figure 3.

Throughout our discussion, Koopmans' theorem is used.[12] That is, an experimental IP is assumed equal to the negative of the corresponding occupied orbital energy, while an experimental electron affinity is equal to the negative of the corresponding vacant orbital energy. Thus, a low IP indicates a high-energy occupied orbital, while a higher IP implies a lower-energy occupied orbital.

Substitution of the electron-donating methoxy group at C-2 in norbornene decreases the IP by 0.82 eV. In the context of Koopmans' theorem,[12] this indicates that the π orbital is desta-

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(10) Fujimoto, H.; Uemura, S.; Miyoshi, H. *Tetrahedron* **1981**, *37*, 55.

(11) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(12) Koopmans, T. *Physica* (*Utrecht*) **1934**, *1*, 104.

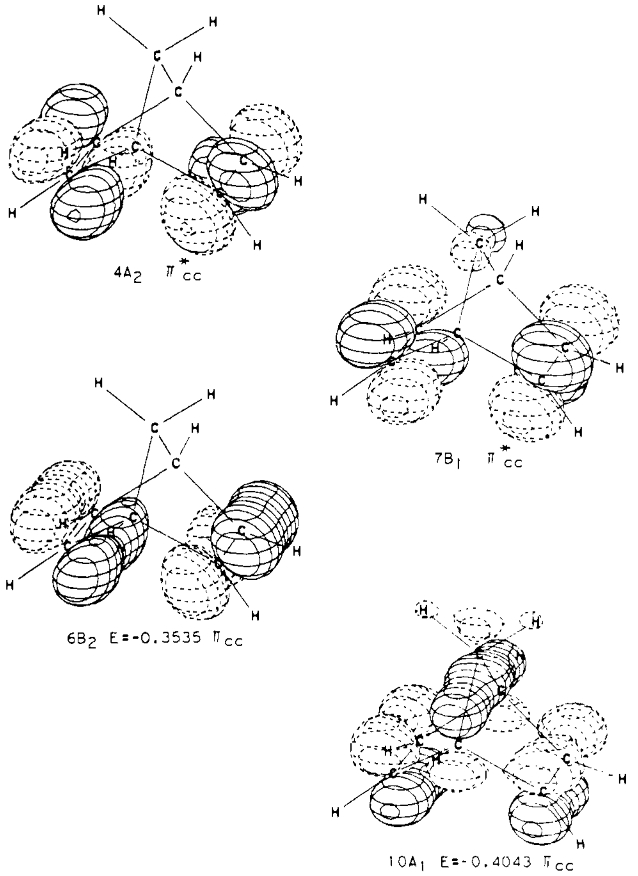

Figure 3. The π orbitals of norbornadiene. (Reproduced by permission from W. L. Jorgensen and L. Salem, "The Organic Chemists' Book of Orbitals"; Academic Press:, New York, 1973.)

bilized by mixing of the π orbital of norbornene with the lower-lying lone-pair orbital on oxygen. Methoxy substitution on norbornadiene lowers the IP's of both π orbitals, but to different extents. The first IP of 2-methoxynorbornadiene (8.05 eV), which arises from the π_- orbital, is 0.64 eV lower than that of norbornadiene. The second IP (9.27 eV), attributable to the π_+ orbital, is only 0.28 eV lower than the second IP of norbornadiene. The difference between the first and second IP's of 2-methoxynorbornadiene (1.22 eV) is 40% greater than this difference (0.86 eV) in norbornadiene. The origin of this disparity is proven later by computations, but a straightforward explanation is possible on the basis of perturbation ideas. The first IP at 8.05 eV must arise from an orbital which resembles the HOMO of 2-methoxynorbornene (IP = 8.15 eV), but which has been further destabilized by 0.1 eV by mixing in an antibonding fashion with the lower-energy norbornene-like π orbital. The second IP (9.27 eV) arises from an orbital which is mainly norbornene-like, but which has been stabilized by 0.3 eV mixing in a bonding fashion with the higher-lying 2-methoxynorbornene-like orbital. Thus, the HOMO is expected to be more concentrated on the methoxyy-substituted double bond than on the remote double bond. The IP of the lone pair on oxygen was not resolved for either 2-methoxynorbornadiene or 2-methoxynorbornene.

The first and second IP's of 2-(trimethylsiloxy)norbornadiene are 8.06 and 9.07 eV, respectively. These IP's arise from highly unsymmetrical π_- and π_+ orbitals, much like 2-methoxynorbornadiene. The trimethylsiloxy group destabilizes the π_- orbital of norbornadiene by the same amount as observed for the methoxy group. However, the second IP of 2-(trimethylsiloxy)norbornadiene is 0.20 eV lower than that of 2-methoxynorbornadiene, and 0.48 eV lower than the second IP of norbornadiene. The difference between the first and second IP's of 2-(trimethylsiloxy)norbornadiene is 1.01 eV, which is smaller than that of 2-methoxynorbornadiene but greater than that of norbornadiene itself. The IP due to the π orbital of 2-(trimethylsiloxy)norbornene (8.09 eV) is identical within experimental error to the first IP of 2-(trimethylsiloxy)norbornadiene. All of these trends are consistent with the assignment of the first IP of (trimethylsiloxy)-norbornadiene to an orbital essentially localized on the substituted double bond, while the second IP is due to a more nearly norbornene-like orbital on the unsubstituted bond. In fact, the second IP of (trimethylsiloxy)norbornadiene is within 0.1 eV of the value of the IP or norbornene.

The photoelectron spectrum of 2-chloronorbornadiene has two distinct bands at 8.77 and 9.68 eV, arising from the π_- and π_+ orbitals. The first and second IP's of 2-chloronorbornadiene are higher than those of norbornadiene by 0.08 and 0.13 eV, respectively. For comparison, the IP of ethylene is lowered by 0.37 eV upon chlorine substitution. In this case lowering is more than compensated for by the π-donor effect. Here, the ethylene π orbital has a large coefficient at the site of chlorine attachment (0.717 by HMO), and the ethylene π and chlorine n_{3p} orbitals are close in energy (10.5 and 11.5 eV, respectively). Both the large coefficient and small energy gap cause the chlorine to destabilize the ethylene π orbital. In norbornadiene, chlorine substitution again has a large inductive orbital energy lowering effect, but here this effect is not overwhelmed by the small π donor effect of the chlorine lone pairs. The relatively small chlorine-donor effect arises from the small norbornadiene π coefficients (0.50 by HMO for both π_- and π_+) and the larger gaps between the norbornadiene π orbital energies (8.69 and 9.55 eV) and that of the chlorine 3p orbital (11.5 eV). Assuming that the π-donor effect is proportional to $c^2/\Delta\epsilon$, where c is the coefficient at the site of substitution and $\Delta\epsilon$ is the orbital energy gap before interaction, the orbital energy raising due to the π-donor effect of Cl should be 1:0.2:0.3 for ethylene, π_-, and π_+ of norbornadiene, respectively. Since both IPs of 2-chloronorbornadiene are affected to the same extent, and the IP gap remains the same as that of norbornadiene, within experimental error, we conclude that the chlorine-substituent effect is transmitted equally to both double bonds. A similar effect has been found in (cyanobenzo)norbornadienes (see below).[14] A third band in the 2-chloronorbornadiene spectrum at 11.17 eV is probably due to ionization from a σ orbital of the norbornadienyl skeleton, while an unresolved band at 11.5 to 11.9 eV may be attributed to the 3p nonbonding atomic orbitals of chlorine. By way of comparison, the vertical IP's corresponding to the n_{Cl} orbitals of vinyl chloride are found at 11.72 and 11.87 eV.[13]

Substitution of a methoxycarbonyl group on norbornadiene raises the first and second IP's by 0.23 and 0.17 eV, respectively. The difference between these IP's (0.80 eV) is essentially identical with that of norbornadiene. The methoxycarbonyl substitutent, like chlorine, stabilizes both orbitals nearly equally, and both orbitals are expected to retain more or less symmetrical π_+ and π_- character. Additional maxima appear in the spectrum at 10.26 and 10.9 eV, which can be assigned to the n_{CO} and n_O orbitals of the ester group. For comparison, the values of the carbonyl IP's of methyl methacrylate are 10.36 and 11.06 eV.[15]

The cyano group in 2-cyanonorbornadiene produces an effect similar to that of the 2-methoxycarbonyl group, but the effect is much greater. Thus, the first IP of the cyano compound (9.26 eV) is 0.57 eV higher than that of norbornadiene. The second IP (10.12 eV) is increased by 0.57 eV compared to norbornadiene, so the $\pi_- - \pi_+$ gap remains 0.86 eV, as it is in the parent diene. This can be attributed to the appproximately equal transmission of the cyano group inductive electron withdrawal to both π bonds. We have previously noted that the three high-energy π orbitals of benzonorbornadiene are all lowered to a similar extent, regardless of the site of attachment of a cyano group.[14]

The influence of the cyano group on the norbornadiene π orbitals (ΔIP = 0.57 eV) is larger than the effect found for at-

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(13) Lake, R. F. *Thompson*, H. *Proc. R. Soc. London, Ser. A* **1978**, *315*, 323. Wittel, K.; Bock, H. *Chem. Ber.* **1974**, *107*, 317.

(14) Paquette, L. A.; Ku, A. Y.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5972.

(15) Van Dam, H.; Oskam, A. *J. Electron Spectrosc. Relat. Phenom.*, **1978**, *13*, 273.

Table III. Coefficients of the p Orbitals in the π Molecular Orbitals (MO's) of 2-Substituted Norbornadienes

	MO's	C atom	norbornadiene	2-methoxy-norbornadiene	2-chloro-norbornadiene	2-formyl-norbornadiene[b]
SLUMO	π_-^*	2	0.59	0.67	0.62	0.18
		3	0.59	0.61	0.54	0.17
		5	0.59	0.51	0.59	0.73
		6	0.59	0.52	0.56	0.72
LUMO	π_+^*	2	0.54	0.49	0.60	0.42
		3	0.54	0.44	0.59	0.62
		5	0.54	0.61	0.49	0.20
		6	0.54	0.60	0.49	0.17
HOMO	π_-	2	0.47	0.44	0.46	0.47
		3	0.47	0.62	0.48	0.48
		5	0.47	0.26	0.42	0.42
		6	0.47	0.26	0.42	0.42
SHOMO	π_+	2	0.41	0.19	0.32	0.34
		3	0.41	0.75	0.34	0.34
		5	0.41	0.54	0.44	0.45
		6	0.41	0.55	0.44	0.44

[a] Since the π orbitals are not perpendicular to a plane of symmetry of the molecule, the π and π^* orbitals have s, p_x, and p_y coefficients. The numbers given in the table are the square roots of the sum of the squares of each coefficient at that carbon. [b] The LUMO has a large π^*_{CO} component, with coefficients of 0.47 and 0.56 on C and O. A third vacant orbital at 11.1 eV is polarized toward the substituted double bond, but oppositely within this bond; coefficients are 2 (0.68), 3 (0.49), 5 (0.26), and 6 (0.32). Essentially, the LUMO and TLUMO are π^*_{CO} orbitals.

tachment of the cyano group to ethylene (ΔIP = 0.40 eV). The cyano group, like the chlorine substituent, has a small conjugative electron-donation effect[16] which is further diminished by virtue of the smaller π coefficients on norbornadiene and the larger gap between its orbtials and the π_{CN} orbital.

The cyano group lowers the π-orbital energies of norbornadiene about three times more than does the methoxycarbonyl group. This is a somewhat larger difference than found for ethylene, where a cyano group lowers the π orbital by 0.4 eV, and the methoxycarbonyl group lowers it by 0.2 eV.[16] The larger difference observed for norbornadiene may be a manifestation of inherently greater inductive electron withdrawal by the cyano group in cases where π-donor effects are negligible.

The spectrum of 2-phenylnorbornadiene shows three distinct low-energy bands. The first and third bands have about equal areas, whereas the second is twice as intense. The first band at 7.97 eV is assigned to the π orbital of the phenyl group (Ph_S), mixed in an antibonding fashion with the norbornadiene π orbitals. This value should be compared with the IP corresponding to the Ph_S–π orbital of *trans*-β-methylstyrene (8.38 eV).[17] The second band at 9.06 eV can be assigned to the overlapping IP's of the π_- orbital of norbornadiene and Ph_A orbital of benzene, which cannot mix with norbornadiene π orbitals owing to the node located at the site of attachment to norbornadiene. The basis for this assignment is provided by *trans*-β-styrene which has an IP of 9.14 eV attributed to the Ph_A orbital.[17,18] The third band at 9.92 eV in the 2-phenylnorbornadiene spectrum is assigned to the norbornadiene π_+ orbital mixed with the Ph_S orbital. It lies ~0.4 eV lower than the π_+ IP of norbornadiene.

This interpretation of this spectrum is clearly more difficult than those described earlier. Nevertheless, because the phenyl group probably does not achieve coplanarity with the attached alkene group, we prefer to assume that the second and third bands arise from the ionization of orbitals which are mainly π_- and π_+ in character. These orbitals are both 0.4 eV lower in 2-phenylnorbornadiene than in norbornadiene.

Electron Affinities. Vertical electron affinities (EA) for norbornadiene and its derivatives were determined by electron-transmission spectroscopy (ETS).[19,20] The accuracy of the measurements is estimated to be ±0.05 eV. The electron affinities are negative, indicating that the anions are unstable with respect to the neutral molecule plus an electron. The first and second EA's of norbornadiene are −1.04 and −2.56 eV, which arise from electron capture by the π_+^* and π_-^* orbitals. These are shown in Figure 3. As for IP's, EA's are interpreted with the aid of Koopmans' theorem.[12] A small negative EA implies a low-lying vacant orbital, while a more negative EA corresponds to a higher-energy vacant orbital.

For norbornadiene, the gap of 1.52 eV between the π EA's is nearly twice as large as the π IP gap. This can be attributed to the overlap of the π^* orbitals being greater than that of the π orbitals because of the larger coefficients on π^* orbitals.[22] Introduction of a methoxy group at C-2 in norbornadiene decreases the first EA by 0.31 and the second by 0.29 eV. In other words, the unoccupied π^* orbitals are destabilized by the methoxy group. The destabilization is less than that observed for the π orbitals, since the energy gap between the π^* orbitals and the n_O orbital is greater than that between the π and n_O orbitals.

Substitution by trimethylsiloxy at C-2 of norbornadiene destabilizes the π_+^* and π_-^* orbitals by 0.11 and 0.21 eV, respectively, which is approximately half that observed for methoxy substitution. While the origin of this difference is difficult to identify, it is possible that the anion-stabilizing effect of silicon,[23] even when one bond removed for the π system, partially overcomes the destabilizing influence of the oxygen lone-pair donor orbital.

Chloro substitution at C-2 lowers the π_+^* and π_-^* orbitals by 0.21 and 0.50 eV, respectively. Once again the inductive electron-withdrawing effect by chlorine predominates over the destabilization arising from the mixing of a chlorine 3p lone-pair orbital with the π^* orbitals. The same general trend has been observed for chloroethylene and chlorobenzene.[24,25] Consequently, the LUMO and SLUMO of 2-chloronorbornadiene are lower in energy than those of norbornadiene.

Molecular Orbitals. Ab initio RHF calculations using the minimal STO-3G basis set[26] were carried out on the parent

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(16) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937.

(17) McAlduff, E. J.; Houk, K. N., unpublished results on styrenes.

(18) Rabalais, J. W. "Principles of Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1977.

(19) Sanche, L.; Schulz, G. J. *Phys. Rev. A* **1972**, *5*, 1672.

(20) Jordan, K. D.; Burrow, P. D. *Acc. of Chem. Res.* **1978**, *11*, 341.

(21) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *Chem. Phys. Lett.* **1976**, *42*, 227.

(22) Staley, S. W.; Giordan, J. C.; Moore, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3638. Burrow, P. D.; Jordan, K. D. *Ibid.* **1982**, *104*, 5647.

(23) Modelli, A.; Jones, D.; Distefano, G. *Chem. Phys. Lett.* **1982**, *86*, 434.

(24) Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D. *Chem. Phys. Lett.* **1981**, *82*, 270.

(25) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *Chem. Phys. Lett.* **1976**, *42*, 227.

(26) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

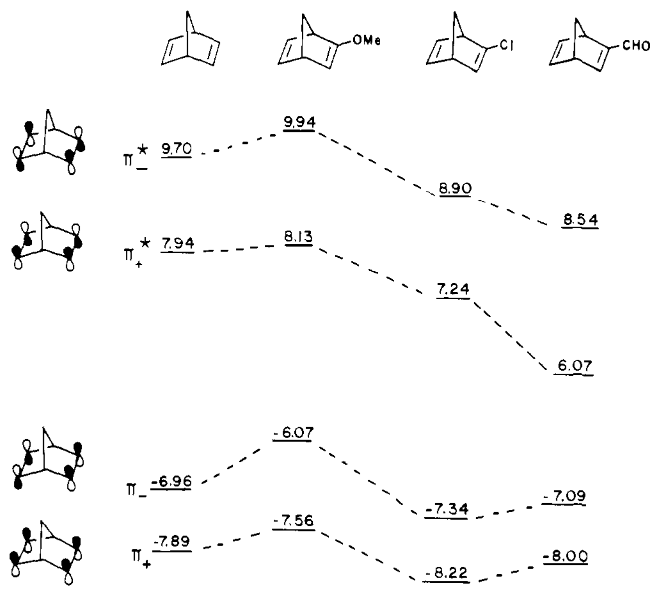

Figure 4. Summary of STO-3G π orbitals of norbornadiene and 2-substituted derivatives.

norbornadiene and several 2-substituted derivatives. The geometry of norbornadiene was the MINDO/3 optimized structure,[27] while standard geometries were employed for the three substituents studied, chloro, formyl, and methoxy, which model halogen, electron-withdrawing, and electron-donating substituents, respectively. The results of these calculations are summarized in Figure 4 and Table III. Using Koopmans' theorem,[12] the calculated occupied orbital energies can be compared with the IP's obtained from photoelectron spectroscopy. Similarly, the theoretical electron affinities (EA)'s can be obtained by using the negative of the virtual orbital energies.

Minimal basis set values of orbital energies yield IP's for the π_- and π_+ orbitals of norbornadienes which are too large by 1.6–1.8 eV, but usually give reasonable IP trends.[6] The electron affinities are grossly underestimated, by about 7 eV. The difference between the calculated IP's of norbornadiene is 0.93 eV, which is in close agreement with the experimental splitting of 0.86 eV. The difference between the two calculated EA's is 1.76 eV, somewhat greater than the experimental difference of 1.52 eV.

Substitution of a methoxy group on norbornadiene lowers the first and second IP's by 0.89 and 0.33 eV according to the STO-3G calculations. By comparison, the experimental IP decreases are 0.64 and 0.28 eV for 2-methoxynorbornadiene and 0.63 and 0.48 eV for 2-(trimethylsiloxy)norbornadiene. Thus, the trends in IP changes are quite well reproduced by calculations. The methoxy group polarizes the highest occupied MO (HOMO) toward the substituted double bond quite markedly (Table III), as deduced earlier. The substituted double bond is also dramatically polarized in the HOMO, while the unsubstituted is not. The polarization of the substituted double bond is like that observed for other donor-substituted alkenes. The changes have been thoroughly rationalized.[28] The second-highest occupied MO (SHOMO) is somewhat polarized toward the unsubstituted double bond, but the substituted double bond is even more polarized than in the HOMO.

The computed lowest unoccupied (LUMO) and second-lowest unoccupied MO (SLUMO) energy changes caused by methoxy substitution are slightly smaller than the experimental values. The LUMO is polarized toward the remote double bond. There is no significant difference between the coefficients at C-5 and C-6, but the coefficient at the substituted carbon atom, C-2, is somewhat larger than the value at C-3, in both the LUMO and SLUMO. These trends correspond to earlier generalizations.[28]

STO-3G calculations correctly predict that 2-chloro substitution raises IP's. However, the theoretical IP's are raised 3–4 times more than is observed experimentally. This exaggeration probably reflects excessive electron withdrawal by chlorine when polarization functions are not included in the basis set.[24] However, the difference between the calculated IP's of the π_- and π_+ orbitals is 0.88 eV, which is close to the experimental difference of 0.91 eV. The fact that the calculations predict too great a stabilization of the π^* orbitals upon chlorine substitution may also be ascribed to similar basis set deficiencies.[24]

The calculated MO coefficients indicate that the HOMO is polarized slightly toward the more substituted double bond. The polarization of the SHOMO is also small and opposite to that of the HOMO. These polarizations are caused by the π-donor effect of Cl. Inductive electron withdrawal by Cl influences both carbons, and does not alter the polarization. The calculations show that the LUMO of 2-chloronorbornadiene is polarized toward the substituted double bond, in contrast to the LUMO of 2-methoxynorbornadiene.

Formyl substitution is predicted to increase the π IP's by only ~0.1 eV, less than the ~0.2 eV observed for methoxycarbonyl substitution and 0.6 eV for cyano substitution. The π-donor effect of formyl is probably slightly overestimated by STO-3G calculations. The huge (1.87 and 1.16 eV) computed lowering of the LUMO's is expected,[28] but we were unable to obtain the ET spectrum, as the molecule was too reactive. The formyl group, like methoxy and chlorine, slightly polarizes the HOMO toward the more substituted double bond and the SHOMO toward the remote double bond, but the effects are smallest for formyl, as expected.[28] The LUMO is strongly polarized toward the more substituted double bond, and this orbital shows the typical polarization expected of a π acceptor.[28] There are actually three π^* orbitals. The LUMO and third LUMO are essentially bonding and antibonding combinations of the carbonyl π^* orbital with the π^* orbital of the attached alkene, while the SLUMO is primarily the π^* orbital of the unsubstituted double bond.

Relationships between Electron Structures and Carbene Selectivities. The preceding description of experimental and computational results provides a reasonably comprehensive picture of the π electronic structures of 2-substituted norbornadienes. Returning to the object of these studies, can we better understand the selectivities observed in carbene cycloadditions to 2-substituted norbornadienes?

To answer this question, we will use the qualitative frontier molecular orbital model which has been so successful in rationalizing other types of cycloaddition selectivities.[28] For difluorocarbene cycloaddition, the interaction of the carbene LUMO with the alkene HOMO constitutes the dominant frontier molecular orbital interaction.[29] Raising the norbornadiene HOMO energy should increase this interaction and accelerate the reaction rate. For multicenter orbitals such as those in norbornadienes, the preferred site of attack of electrophilic carbenes will be the site of larger HOMO coefficients, in order to maximize HOMO-LUMO overlap.[28] On the other hand, it has been proposed that the homo-1,4 cycloaddition is the result of carbene HOMO, norbornadiene LUMO interaction.[30] If such were the case, then the EA's of the norbornadienes should correlate with the extent of homo-1,4 cycloadditions. Although there is an apparent trend in this direction, we will show that the homo-1,4 cycloaddition is slowed by electron withdrawers, but to a smaller extent than the exo cycloaddition is decelerated.

Beginning first with the exo-1,2 cycloaddition syn/anti selectivity, the trends shown in the second and third columns of Table I are in full accord with the results of the STO-3G calculations, which show that all substituents cause the HOMO to be concentrated on the substituted double bond carbons. Donors, such as methoxy and trimethylsiloxy, and the conjugating substituent,

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(27) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307. Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *Ibid.* **1975**, *97*, 1311. Details of geometry are available on request from K.N.H.

(28) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

(29) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(30) Jean, Y. *Tetrahedron Lett.* **1977**, 2689. Jefford, C. W.; de los Heros, V.; Gehret, J. C. E.; Wipff, G. *Ibid.* **1980**, 1629.

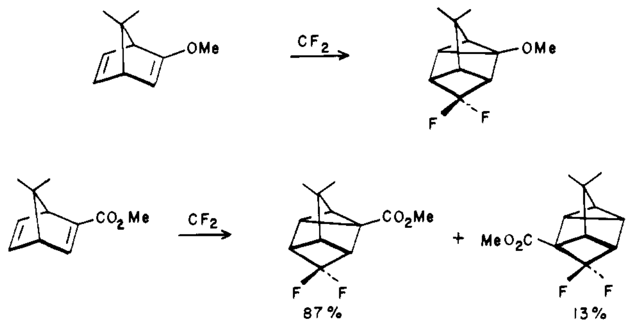

Figure 5. Reactions of difluorocarbene with 2-substituted 7,7-dimethylnorbornadienes.

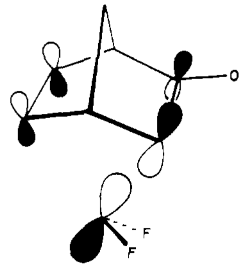

Figure 6. Orbital interactions involved in the homo-1,4 cycloaddition. The HOMO of a donor-substituted norbornadiene and the LUMO of difluorocarbene are shown.

phenyl, cause the greatest imbalance in HOMO coefficients. Indeed, these norbornadiene derivatives give the most syn-1,2 cycloaddition product (75–89%). The reason that the trimethylsiloxy derivative gives some of the anti adduct is not clear. Chlorine produces less syn polarization of the HOMO, and a 15.5:1 ratio of syn/anti-1,2 adduct is observed. Electron-withdrawing substituents produce the least polarization (Table III), and have only a slight preference for syn addition; for CO_2Et, CO_2Me, and CN, the syn/anti-1,2 ratios are 3.7:1, 2.5:1, and 1.5:1.

For the homo-1,4 cycloadditions, all 2-substituted norbornadienes give predominantly the anti adducts. Only in the case of 2-cyanonorbornadiene, and perhaps 2-(trimethylsiloxy)norbornadiene, are any syn-homo-1,4 adducts observed. Before discussing these results, a brief discussion of the electronic nature of this reaction is pertinent.

Although the homo-1,4 cycloaddition of carbenes to norbornadiene was initially thought to involve nucleophilic attack on the homo-diene,[30] an orbital symmetry-allowed process, Klumpp and Kwantes[31] showed that the rates of homo-1,4 cycloadditions respond to changes in substituent at C-7 in norbornadienes in the same way as the exo-1,2 cycloadditions. As both rates are diminished by π acceptors at C-7 then both reactions are electrophilic.[31]

We devised a more sensitive test using 2-substituted-7,7-dimethylnorbornadiene.[32] The exo face of these molecules is sterically blocked; only endo-1,2 and homo-1,4 cycloadditions are observed. The relative rates of reactions of difluorocarbene to 2-methoxy-7,7-dimethylnorbornadiene, 7,7-dimethylnorbornadiene, and 2-(methoxycarbonyl)-7,7-dimethylnorbornadiene are 2.6:1.0:0.045.[32] The 2-methoxy derivative gives only the anti-homo-1,4 adduct, whereas the 2-methoxycarbonyl compound gives the anti- and syn-homo-1,4 cycloadducts in a 6.7:1 ratio (Figure 5). Thus, the homo-1,4 cycloaddition is electrophilic, and the same trend toward lesser homo-1,4 selectivity is observed for electron-withdrawing groups as is found for exo-1,2 additions to norbornadienes.

The strong preference for anti-homo-1,4 cycloaddition is readily explicable in terms of the HOMO coefficients. Thus, in the transition state for this reaction, the carbene LUMO should interact most strongly at the site of largest HOMO coefficient, which is always at C-3. Figure 6 shows this pictorially. This transition state collapses to the anti adduct. For electron-withdrawing substituents, the HOMO C-2–C-3 polarization is smallest, and less selectivity is observed.

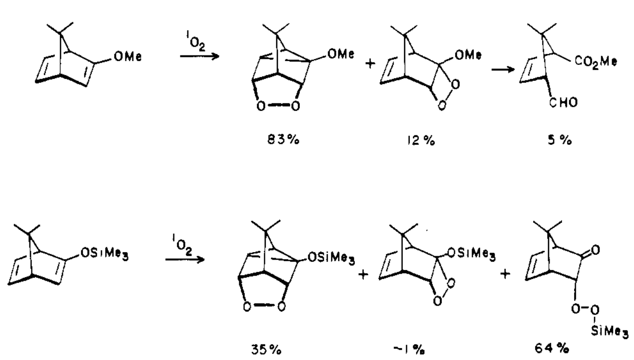

Figure 7. Reactions of singlet oxygen with 2-donor-substituted norbornadienes.

Table IV. Cycloaddition Selectivities and Ionization Potentials

	R =						
	MeO	Me_3SiO	Ph	H	Cl	CO_2Me	CN
1,2:homo-1,4	8.1	4.2	3.0	1.9	1.9	1.1	1.4
IP (eV)	8.05	8.06	(8.51)[a]	8.69	8.77	8.92	9.26

[a] The average of the first and second IP's of 2-phenylnorbornadiene has been used.

Finally, we turn to the thorniest problem, the variations in exo-1,2/endo-homo-1,4 ratios as the 2-substituent is varied. As noted in the last column of Table I, the ratio decreases progressively as the substituent is made more electron withdrawing. Put in less qualitative terms, there is a nearly regular correspondence between an increase in IP and a decrease in the 1,2:homo-1,4 ratio as shown in Table IV.

Superimposed on this changing ratio is the expectation that the overall rate of reaction decreases in the same order. Exo-1,2 cycloaddition should be retarded to a greater extent by the decrease in electron-richness of the norbornadiene, while the endo-homo-1,4 cycloaddition will be less influenced. Such a trend has been observed previously for dichlorocarbene cycloadditions to 7-substituted norbornadienes[31] and for Diels–Alder cycloadditions of hexachlorocyclopentadiene to 7-substituted norbornadienes.[5]

The decrease in rate of exocycloaddition follows theoretical expectations: as the HOMO is lowered, interaction with the carbene LUMO diminishes, and the stabilization of the transition state decreases. Why are the rates of endo cycloadditions influenced less by changes in the HOMO energy than the rates of exocycloadditions? In a forthcoming publication,[33] we will develop the hypothesis that endo cycloadditions are less sensitive than exo cycloadditions because the hindering, eclipsing interactions which develop between the endo-forming bonds and allylic CC bonds are somewhat alleviated when the norbornadiene skeleton has electron-withdrawing substituents. In any case, the decreasing exo/endo ratio is in accord with the patterns observed for other electrophilic additions.

It is worth mentioning here that other reagents, namely singlet oxygen, behave as electrophilic species toward 2-methoxy and 2-trimethylsiloxy norbornenes and norbornadienes.[8,34] The rates of addition to the nonsubstituted parent olefins are extremely slow, requiring several hours for reaction.[35] Electron-donating 2-substituents cause reactions with singlet oxygen to occur within the span of 30 min. The product compositions shown in Figure 7 reflect the large magnitude of the HOMO coefficients on the C-3 positions of 2-donor norbornadienes.

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(31) Klumpp, G. W.; Kwantes, P. M. *Tetrahedron Lett.* **1981**, 831.

(32) Jefford, C. W.; Phan Thanh, Huy *Tetrahedron Lett.* **1982**, 391.

(33) Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Nagase, S.; Mazzochi, P. A., submitted for publication.

(34) Jefford, C. W.; Rinbault, C. G.; Kohmoto, S., unpublished work.

(35) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1974**, *57*, 2257.

J. Am. Chem. Soc. **1983**, *105*, 5569-5576 5569

Summary. We have shown how the energies and shapes of the frontier molecular orbitals of 2-substituted norbornadienes, derived from a combination of experimental and theoretical evidence, rationalize the selectivities observed in carbene cycloadditions to these species. These quantities should be useful in predicting the course of other electrophilic, as well as nucleophilic, and radical reactions.

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Registry No. Norbornadiene, 121-46-0; 2-methoxynorbornadiene, 74437-38-0; 2-(trimethylsiloxy)norbornadiene, 68364-22-7; 2-chloronorbornadiene, 2294-41-9; 2-cyanonorbornadiene, 39863-20-2; 2-(methoxycarbonyl)norbornadiene, 3604-36-2; 2-phenylnorbornadiene, 74437-39-1; norbornene, 498-66-8; 2-methoxynorbornene, 17190-90-8; 2-(trimethylsiloxy)norbornene, 57722-40-4.

Magnetic Susceptibility Anisotropy, Molecular *g* Values, and Other Molecular Properties of Cyclopropane As Determined from Rotational Zeeman Studies of the Cyclopropane–H^{35}Cl and Cyclopropane–HC^{15}N Complexes

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Abstract: A pulsed, Fourier-transform microwave spectrometer has been used to observe the rotational Zeeman effect with the cyclopropane–HCl and cyclopropane–HCN complexes. The molecular *g* values and magnetic susceptibility anisotropies have been determined for the cyclopropane–HCl complex and have been used to obtain the molecular quadrupole moment, magnetic susceptibility tensor elements as well as the paramagmetic and diamagnetic contributions, and the second moment of the electronic charge distribution. Certain Zeeman parameters along with zero-field rotational constants have been obtained for cyclopropane–HC^{15}N. The Zeeman constants for both complexes have then been used to extract various magnetic properties of cyclopropane.

Introduction

Microwave Zeeman experiments have been shown to be quite effective in the determination of certain molecular information. The molecular quadrupole moment, molecular *g* values, magnetic susceptibility anisotropies, and the sign and magnitude of the electric dipole moment can all be obtained by this means.[1,2] The molecular quadrupole moment and electric dipole moment give important information regarding charge distribution. The molecular *g* values can be combined with magnetic susceptibility anisotropies, structural information, and bulk susceptibility to give the second moments of the electronic charge distribution as well as the diamagnetic and paramagnetic contributions to the magnetic susceptibilities. In the case of ring compounds, the magnetic susceptibilities can be compared to localized semiempirical models to give a criterion for aromaticity and delocalization.[3] Obtaining this information from microwave Zeeman experiments is, however, contigent upon the molecule having a permanent electric dipole moment, thus allowing rotational transitions to be observed. In the case of a nonpolar molecule it is conceivable that weak complexation with a dipolar molecule might, however, indirectly give information about the nonpolar binding partner through Zeeman studies. The development of pulsed, Fourier-transform microwave spectroscopy with gas pulsed into a Fabry–Perot cavity,[4] and more recently, Zeeman microwave studies under the same conditions[5-7] make this sort of experiment feasible. Recently, this laboratory has been involved in Zeeman studies of many linear hydrogen-bound complexes with the aim of determining the effects of weak complexation upon the molecular properties of the substituent molecules.[7] The results have shown that if proper account is taken of changes in centers of mass and bending modes introduced upon complexation, the molecular quadrupole moments, magnetic susceptibility anisotropies, and *g* values are all to a good approximation resultants of the corresponding properties in the substituent molecules. It then seems plausible to study the aforementioned molecular properties of cyclopropane by obtaining the same molecular properties for cyclopropane complexed with a dipolar binding partner and subtracting out the effects of the binding partner. By complexing cyclopropane with two very magnetically different molecules, H^{35}Cl and HC^{15}N, the ability of the projection equations to subtract out the effects of the binding partners can be tested.

Cyclopropane has been the object of much study and speculation. Values are not known for the molecular quadrupole moment. In addition, proton shieldings by cyclopropyl groups have pointed to cyclopropane as having an unexpectedly large magnetic susceptibility anisotropy possibly arising from the presence of ring currents.[8-12] Bulk susceptibility measurements of cyclopropane have caused similar speculations.[13] Ring currents have been attributed to many aromatic compounds.[3,14,15] and though there is disagreement[16-18] it is thought that many ring compounds not

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(1) C. H. Townes, G. C. Douismanis, R. L. White, and R. F. Schwarz, *Discuss. Faraday Soc.*, **19**, 56 (1955).

(2) W. H. Flygare, *Chem. Rev.*, **74**, 653 (1974).

(3) T. G. Schmalz, C. L. Norris, and W. H. Flygare, *J. Am. Chem. Soc.*, **95**, 7961 (1973).

(4) T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.*, **52**, 33 (1981).

(5) W. G. Reed and E. J. Campbell, *Phys. Rev. Lett.*, **49**, 1146 (1982).

(6) E. J. Campbell and W. G. Reed, *J. Chem. Phys.*, in press.

(7) W. G. Reed and E. J. Campbell, *J. Chem. Phys.*, in press.

(8) K. P. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(9) J. Burke and P. Lauterbur, *J. Am. Chem. Soc.*, **86**, 1870 (1964).

(10) C. Poulter, R. Boiken, J. Braumm, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2291 (1972).

(11) R. C. Hahn and P. C. Howard, *J. Am. Chem. Soc.*, **94**, 3143 (1972).

(12) D. J. Patel, M. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(13) J. R. Lacher, J. W. Pollock, and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).

(14) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

(15) C. Johnson and F. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(16) J. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

(17) J. Musher, *J. Chem. Phys.*, **46**, 1219 (1967).

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