the two isomers approaching 30 kcal/mol.

Finally, reaction 16 is the bond separation reaction for benzene. As it reflects the deviation of additivity from single and double bond energies, the bond separation energy has been suggested as one possible measure of the resonance energy of benzene.[3] The bond separation energy is large and positive and is moderately well reproduced by Hartree-Fock theory. MINDO/3 does give a positive value but only a small fraction of the observed magnitude.

In view of the considerable parameterization[7] in MINDO/3, the extent of these deficiencies is remarkable. One possibility is that optimum parameterization has still not been achieved. BDL doubts this, remarking that "we think it likely that MINDO/3 represents the limit attainable by an INDO-based semiempirical treatment". We have had similar experience in this laboratory. Some years ago an attempt was made to develop a CNDO theory (complete neglect of differential overlap) parameterized directly on experimental energies but was abandoned because it proved impossible to obtain correct single, double, and triple bond energies with the same parameters. It seems likely that the underlying mathematical structure of CNDO/INDO theory cannot accommodate these energetic relationships whatever the parameterization. The possibility remains, as BDL point out, that a more sophisticated semiempirical theory with a structure simulating some higher level of ab initio theory, may yet achieve the objective of providing an inexpensive and reliable mathematical model for hydrocarbon chemistry. For the present, however, MINDO/3 clearly suffers many disadvantages that can be avoided if sufficiently flexible ab initio Hartree-Fock treatments are used.

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(7) For hydrocarbons there are nine adjustable parameters in MINDO/3 (ξ_s (C), ξ_p (C), ξ_s (H), B_{HH}, B_{CH}, B_{CC}, α_{HH}, α_{CH}, α_{CC}).

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MINDO/3. An Evaluation of Its Usefulness as a Structural Theory

Sir:

In the preceding communication[1] Pople has conclusively documented that the recently introduced version of Dewar's MINDO method (MINDO/3)[2] fails to account properly for a wide variety of key energetic relationships involving polyatomic hydrocarbons. Furthermore he has pointed out that these same quantities are quite satisfactorily calculated by the ab initio Hartree-Fock model, given a sufficiently flexible basis set. Pople stresses his opinion that the underlying mathematical structure of CNDO/INDO type theories,[3] those on which Dewar's method is grounded, is intrinsically incapable of dealing adequately with such relationships, independent of exact choice of parameterization. Thus, even though MINDO/3 represents a considerable saving in computation effort over full Hartree-Fock treatments,[4] it must be considered far too unreliable for use as a general theory of chemical bonding.

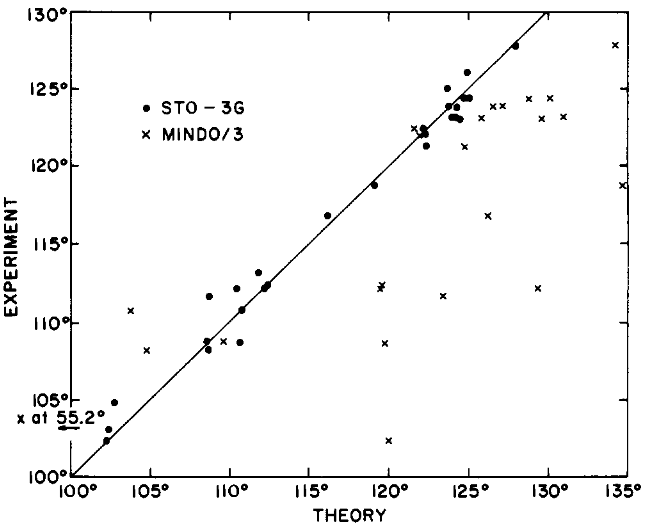


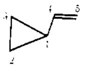
Figure 1. Calculated MINDO/3 (×) and STO-3G (●) vs. experimental skeletal bond angles.

In this manuscript we seek to point out major deficiencies in the ability of the MINDO/3 method to calculate molecular equilibrium geometries, and at the same time to indicate that such failings are not present to a comparable extent in ab initio Hartree-Fock treatments even at the minimal basis set level. Singled out for discussion are bond angles involving the heavy atom skeleton, the aspect of a molecule's equilibrium geometry which most characterizes its gross structure. Comparison of such bond angles calculated using the MINDO/3 and STO-3G[5] methods with experimental values is presented in Figure 1. The data from which it was constructed are listed in Table I. We have attempted to make comparison of the MINDO/3 and STO-3G methods as unbiased as possible. Thus, all skeletal angles of every molecule whose equilibrium geometry has been calculated by both schemes have been considered. In a few cases (formic acid, CF_2, CF_3, and carbonyl fluoride) the reported MINDO/3 geometry is incomplete with regard to specification of the skeletal bond angle (or is missing altogether) although other calculated properties are discussed in text. In these instances we have included comparison between the STO-3G data and experiment.

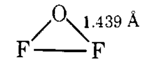
The following points are worthy of mention. Mean deviation of MINDO/3 calculated skeletal bond angles from experiment is 8.7° (23 comparisons). The mean error at the STO-3G level for the same set of compounds (27 comparisons) is only 0.8°,[6] an order of magnitude smaller. The largest difference between an STO-3G and experimental skeletal bond angle is 3.0°. More than a quarter of the comparisons made using MINDO/3 are in error by almost four times that amount, the greatest deviation being 47.9°. Certainly Dewar's statement about geometry comparisons[2] "Such errors are not of great chemical significance and attempts to reproduce geometries much more accurately than this are not of any real value" does not apply here.

Whereas bond angles involving one or two hydrogens in small molecules such as NH_3 and H_2O are fairly well reproduced by MINDO/3, the degree to which the skeletal geometry responds to substitution is vastly overestimated. For example, experimentally the angle about oxygen opens up approximately 7° in going from water to dimethyl ether, and diminishes only slightly (by 1.4°) as both hydrogens are replaced by fluorine atoms. The MINDO/3 calcula-

Table I. Comparison of MINDO/3, STO-3G, and Experimental Skeletal Bond Angles (deg)

Molecule	Angle	MINDO/3[a]	STO-3G	Expt[b]
Propane	CCC	119.6	112.4[c]	112.4
trans-N-Butane	CCC	119.5	112.2[d]	112.2[e]
Isobutane	CCC	103.8	110.8[d]	110.8[f]
Propene	CC=C	128.9	125.1[c]	124.3
Isobutene	CC=C	121.7	122.2[d]	122.4
trans-2-Butane	CC=C	129.6	124.5[d]	123.0[g]
cis-2-Butene	CC=C	134.3	128.0[d]	127.8[h]
trans-1,3-Butadiene	CC=C	131.0	124.2[i]	123.1[j]
Prop-1-yne-3-ene	CC=C	125.9	124.0[i]	123.1[k]
trans-Vinylcyclopropane	CC=C	127.2	123.8[l]	123.8[m]
	$C_2C_1C_4$	134.7	119.1[l]	118.7[m]
Dimethylamine	CNC	129.4	110.5[n]	112.2
Trimethylamine	CNC	119.8	110.7[n]	108.7
Ozone	OOO	126.1	116.2[o]	116.8
Dimethyl ether	COC	123.4	108.7[n]	111.7
Acetaldehyde	CC=C	130.1	124.8[p]	124.4[q]
Glyoxal	CC=O	124.8	122.4[p]	121.2[r]
Acetone	CC=O	122.0	122.3[p]	122.0[s]
Formic acid	OC=O	—	123.7[p]	125.0[t]
Formamide	NC=O	126.6	124.3[p]	123.8
Methylene fluoride	FCF	104.8	108.7[o]	108.3
Fluoroform	FCF	109.6	108.6[o]	108.8
Difluoromethylene	FCF	—	102.7[n]	104.9[u]
Trifluoromethyl radical	FCF	—	111.9[n]	(113.1)[v]
Trifluoroamine	FNF	120.0	102.3[o]	102.4
Oxygen difluoride	FOF	55.2	102.4[o]	103.1
Carbonyl fluoride	FC=O	—	125.0[p]	126.0

[a] Reference 2. [b] Unless otherwise noted experimental bond angles are from: W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Wiley-Interscience, New York, N.Y., 1970. [c] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 93, 5339 (1971). [d] L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, 92, 4786 (1970). [e] K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 32, 748 (1959). [f] R. L. Hilderbrandt and J. D. Wieser, *J. Mol. Struct.*, 15, 27 (1972). [g] B. P. Stoicheff, *Adv. Spectrosc.*, (1959). [h] T. N. Sarachman, *J. Chem. Phys.*, 49, 3156 (1968). [i] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, in press. [j] W. Haugen and M. Traetteberg, *Sel. Top. Struct. Chem.* 113 (1967). [k] T. Fukuyama, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, 42, 379 (1969). [l] W. J. Hehre, *J. Am. Chem. Soc.*, 94, 6592 (1972). [m] A. de Meijere and W. Lüttke, *Tetrahedron*, 25, 2047 (1969). de Meijere and Lüttke present two structures consistent with their electron diffraction measurements. We have already commented (see footnote *l*) that our theoretical structure is in excellent agreement with one of these, regarding the angles C=CC and $C_2C_1C_4$ and the bond length $C_1—C_4$, but not with the other. Thus, we favor it as the equilibrium structure of vinylcyclopropane. Bond angles for the alternative structure are as follows: C=CC, 120.1°; $C_2C_1C_4$, 126.2°. [n] W. J. Hehre, unpublished calculations. [o] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* 52, 4064 (1970). [p] J. E. Del Bene, G. T. Worth, F. T. Marchese, and M. E. Conrad, *Theor. Chim. Acta*, 36, 195 (1975). [q] T. Iijimi and S. Tsuchiya, *J. Mol. Spectrosc.*, 44, 88 (1972). [r] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, 1, 463 (1967–1968). [s] T. Iijima, *Bull. Chem. Soc. Jpn.*, 45, 3526 (1972). [t] J. Bellet, C. Samson, G. Steenbeckeliers, and R. Wertheimer, *J. Mol. Struct.*, 9, 49 (1971); J. Bellet, C. Samson, G. Steenbeckeliers, R. Wertheimer, and A. Deldalle, *ibid.*, 9, 65 (1971). [u] F. X. Powell and D. R. Lide, *J. Chem. Phys.*, 45, 1067 (1966); C. W. Mathews, *Can. J. Phys.*, 45, 2355 (1967). [v] Based on the average of the two experimental estimates: 111.1°, R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 43, 2704 (1965); 115.1°, D. E. Milligan and M. E. Jacox, *ibid.*, 48, 2265 (1968).



tions show the bond angle in the ether to be 123.4° (almost 20° greater than that in H_2O) while the geometry of F_2O is suggested to be that of a three-membered ring. MINDO/3 also fails to describe the experimentally observed changes to the geometry of ammonia which result from substitution. Hence, NF_3, rather than being the planar molecule that Dewar's scheme would have, is actually slightly more puckered than the parent itself. The heavy atom skeleton of trimethylamine is also suggested to be (nearly) planar by the MINDO/3 calculations (∠CNC = 119.8 vs. 108.7° experimentally). Similarly, the central bond angle in dimethylamine comes out vastly too large (129.4° as compared to an experimental value of 112.2°). In all these instances the STO-3G results are in reasonable accord with the experimental data.

Even in the calculation of the gross structure of hydrocarbons does MINDO/3 fare badly. Thus, the theory's prediction of the central angle in propane is far greater than the experimental value (119.6 vs. 112.4°), while that in isobutane is much smaller than observation would have (103.8 vs. 110.8° experimentally). Similarly, the skeletal bond angles in propene, *cis*- and *trans*-2-butene, and 1,3-butadiene are sizably larger than the experimental values (by 4.6–7.9°), while that in isobutene (∠CC=C) is actually smaller. Here again, agreement between the STO-3G data and experiment is excellent.

In conclusion, it is apparent that the considerable parameterization to which Dewar has subjected MINDO/3—including direct calibration to experimental bond angles—has not succeeded in producing a complete and reliable structural theory. In particular, skeletal structures of polyatomic molecules, calculated using MINDO/3 seem to be subject to considerable error and are often times totally absurd. We do not subscribe to Dewar's contention[2] that "the available evidence would seem to suggest that MINDO/3 may provide a better overall quantitative guide to chemical behavior than even good (ab initio Hartree-Fock) calculations." Rather, along with Pople, we stress that the considerable deficiencies plaguing MINDO/3 are of lesser consequence in full ab initio Hartree-Fock treatments. In the case of the calculation of molecular equilibrium geometry it would appear that even the simplest minimal basis set theories offer a reliable and widely applicable alternative.

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The Mixed Valence State Based on μ-Cyanogen-bis(pentaammineruthenium)

Sir:

Binuclear complexes of ruthenium with cyanogen as the bridging ligand have been synthesized. The properties of the mixed valence complex, $[(NH_3)_5RuNCCNRu(NH_3)_5]^{5+}$, are consistent with Robin and Day[1] class III behavior, in contrast to the properties of the analogous pyrazine[2] and 4,4′-bipyridine[3] bridged mixed valence rutheniumammine complexes.

In preparing the μ-cyanogen complex a stoichiometric amount of an aqueous saturated cyanogen solution (~0.2 *M*) was added dropwise to $[(NH_3)_5Ru(OH_2)]^{2+}$ generated in water at pH 4. After 2 hr under an argon atmosphere, the [4+] binuclear complex was precipitated by the addition of sodium bromide or sodium tosylate. Anal. Calcd for $[(NH_3)_5RuNCCNRu(NH_3)_5]Br_4$: C, 3.2; H, 4.03; N, 22.63; Ru, 27.7. Found: C, 2.96; H, 3.93; N, 21.6; Ru, 25.8.[4]

Cyclic voltammetry at 200 mV/sec in 0.1 *M* HCl shows a reversible one electron oxidation of the [4+] complex at 0.71 V and a chemically irreversible (reduction wave absent) one electron oxidation at 1.25 V, both referred to NHE (cf. Figure 1). Ruthenium(III) has been shown to catalyze the hydration of nitriles to amides.[5] Stretching frequencies characteristic of amides are observed in the oxidized samples of the cyanogen complex, and the irreversibility referred to is ascribable to nitrile hydration. To avoid this reaction, DMSO was used with 0.1 *M* $(C_2H_5)_4NClO_4$ as the electrolyte. In this medium, the second oxidation is not observed within the anodic limits of the solvent mixture. A lower limit on the potential difference between the first and second stages of 0.80 V is set by the electrochemistry in DMSO. The lower limit for the conproportionation constant K_{con} from this difference is 10^{13}, to be compared to 1.3×10^6 for the μ-pyrazine[2,6] and $4 < K_{con} < 20$ for the μ-bipyridine system.[3]

The [4+] ion shows a band at 360 nm ($\epsilon = 6.9 \times 10^4$ M^{-1} cm^{-1}) which can reasonably be assigned to the πd–π* transition; for the mononuclear Ru(II) complex the band is at 300 nm ($\epsilon = 2.3 \times 10^4$ M^{-1} cm^{-1}).

In common with most mixed valence complexes of this series, the [5+] ion has a near-infrared transition. Here, as is also the case with the μ-pyrazine ion,[2] the absorption maximum is virtually independent of the solvent (1430, 1480, 1450, 1450 nm in D_2O, CH_3CN, DMF, and DMSO, respectively). The band is very weak ($\epsilon = 4.1 \times 10^2$ M^{-1} cm^{-1} in DMF) and is narrower than is expected on the basis of the equation given by Hush[7] ($\Delta\nu_{1/2}$ = 1.61 kK compared to a calculated value of 4.0 kK).

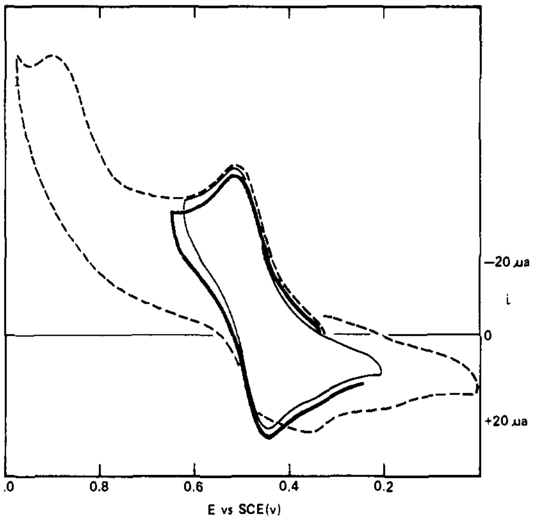

Figure 1. Cyclic voltammogram of $(NH_3)_5RuNCCNRu(NH_3)_5{}^{4+}$ in 0.1 *M* HCl at 200 mV/sec on platinum electrode. In solid curve, the anodic scan was reversed after the potential for the [4+]/[5+] couple was passed.

Examination of the CN stretching frequencies sets a lower limit on the rate of electron transfer in the mixed valence species. The [4+] salts (KBr pellet) exhibit a single CN stretch at 1960 cm^{-1} in the ir and a single one in the Raman at 2185 cm^{-1}, a pattern which, apart from overtones and combination bands, the free ligand also exhibits.[8] The mononuclear complex exhibits two ir active bands at 2220 and 2090 cm^{-1}. Oxidation of the [4+] tosylate salt in DMF with $Fe(bipy)_3(ClO_4)_3$ or with Br_2 yields the [5+] complex with a single ir active band at 2210 cm^{-1}.[9] Contact of the [4+] bromide with liquid Br_2 produces a solid showing a new band at 2330 cm^{-1} in addition to the 2210-cm^{-1} band, these appearing at varying intensity ratios in different preparations. Though the stoichiometry of the reaction is difficult to control, the new frequency can reasonably be assigned to the [6+] state. Since the mixed valence species shows a single ir stretch, which differs from that of cyanogen bound only to Ru(II) (1960 cm^{-1}) or to Ru(III) (2330 cm^{-1}) electron transfer must be rapid compared to the frequency difference of 365 cm^{-1} or $>10^{13}$ sec^{-1}.

Valence delocalization in the mixed valence species is strongly suggested by the chemical behavior. By monitoring the disappearance of the near-ir transition, the rate of decomposition of the [5+] ion was determined to be 7×10^{-3} sec^{-1} in 0.12 *M* DCl-D_2O at 25°. The lower limit for the rate of hydration of the $(NH_3)_5RuNCCN^{3+}$ complex was found to be 10^2 sec^{-1} by cyclic voltammetry[10] and that of the [6+] μ-cyanogen species appears to be as great (an exact value for the binuclear is difficult to obtain because of the large background current). The slower rate of hydration of the mixed valence species by a factor in excess of 10^4 demonstrates that the mixed valence ion is far from showing 3+ ruthenium character. We conclude therefore that the valences are extensively delocalized in the species. The point has been made to us by Professor D. Dolphin, and quite correctly, that the interpretation of the chemical evidence is ambiguous. The decrease in rate registered for the mixed valence species may simply reflect the effect of Ru(II) on the bridging ligand. The chemical evidence is more convincing when, as in the test applied by Isied (ref 2) to the Creutz ion, nonbridging ligand positions are dealt with.