(1972); (k) H. Matsukubo and H. Kato, *J. Chem. Soc., Chem. Commun.*, 412 (1974); (l) W. Steglich, E. Buschmann, and O. Hollitzer, *Angew. Chem., Int. Ed. Engl.*, **13,** 533 (1974). For examples of 1,2-oxazin-6-ones: (m) E. P. Kohler and R. C. Goodwin, *J. Am. Chem. Soc.*, **49,** 219 (1927); (n) T. Ajello and S. Cusmano, *Gazz. Chim. Ital.*, **70,** 512 (1940); (o) C. Armengaud, *C. R. Acad. Sci.*, **254,** 3696 (1962); (p) M. Prasad and C.-G. Wermuth, *ibid.*, **264,** 405 (1967); (q) T. Severin, P. Adhikary, and I. Schnabel, *Chem. Ber.*, **102,** 1325 (1969). For 1,4-oxazin-2-ones: (r) E. Biekert and J. Sonnenbichler, *Chem. Ber.*, **95,** 1460 (1962); (s) K. Dickoré, K. Sasse, and K.-D. Bode, *Justus Liebigs Ann. Chem.*, **733,** 70 (1970); (t) W. Gauss and H. Heitzer, *ibid.*, 59 (1970).

(2) Derivatives of this system have been prepared by G. Seybold, U. Jersak, and R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **12,** 847 (1973); B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, 19 (1973).

(3) G. Maier, *Angew. Chem., Int. Ed. Engl.*, **13,** 425 (1974), has described preliminary experiments with 1,3-oxazin-6-ones directed toward the synthesis of azacyclobutadiene.

(4) Condensation of α-pyrone with dienophiles leads to cyclohexa-1,3-diene intermediates, see H. Behringer and P. Heckmaier, *Chem. Ber.*, **102,** 2835 (1969); J. A. Reed, C. L. Schiling, Jr., R. F. Tarvin, T. A. Rettig, and J. K. Stille, *J. Org. Chem.*, **34,** 2188 (1969), and references cited therein.

(5) J. Terpinski and J. Dabrowski, *J. Mol. Struct.*, **4,** 285 (1969).

(6) A. V. Stavrovskaya, T. V. Protopopova, and A. P. Skoldinov, *Zh. Org. Khim.*, **9,** 699 (1973), report only a melting point for **2.**

(7) In a typical experiment, 1 ml of a 9% solution of **2** in benzene was injected (0.5 drop/sec) into a quartz tube (55 × 0.9 cm) with a nitrogen flow (30 cm^3/min). **1** was separated from the pyrolysate (which contained undecomposed **2,** 1–2% ethyl carbamate, and an as yet unidentified component), by gas chromatography (5 ft × 0.25 in., 15% SE-30 on 80/100 Chromosorb W at 80°).

(8) The yield, which has not been optimized, was based on unrecovered **2** and was sensitive to the surface of the pyrolysis tube.

(9) The iminolactone **2** is very sensitive to moisture and did not consistently give reproducible values of the ultraviolet spectral parameters. The extinction coefficient is an average of several experiments (±20%).

(10) In support of this hypothesis, Kricheldorf[1l] has reported the facile isomerization of a β-isocyanatoacrylate to an alkoxy-1,3-oxazin-6-one.

(11) Steglich et al.[1l] have furnished examples of thermal conversions of derivatives of **9** to 1,3-oxazin-6-ones.

(12) Hydrogen shifts, as formulated for **7** to **8**, have been proposed by W, H. Pirkle, H. Seto, and W. V. Turner, *J. Am. Chem. Soc.*, **92,** 6984 (1970); W. H. Pirkle and W. V. Turner, J. Org. Chem., **40,** 1617 (1975).

(13) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am Chem. Soc.*, **95,** 244 (1973); R. G. S. Pong and J. S. Shirk, *ibid.*, **95,** 248 (1973).

(14) These results parallel an earlier report by Maier[3] of a derivative of **1.**

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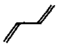
Concerning Criticisms of MINDO/3 by Pople[1] and Hehre[2]

Sir:

Pople[1] bases his criticisms of MINDO/3[3] on calculated heats of reaction for 16 processes, mostly artificial, in 11 of which the errors in the MINDO/3 values are large. This is not surprising since they involve three compounds (CH_4, $C(CH_3)_4$, $CH_3C{\equiv}CCH_3$) for which the errors in the MINDO/3 heats of formation are unusually great. Since we not only tabulated the errors in our papers but also drew specific attention to them in the text,[4] it is not clear to us what further point Pople is trying to make.

The Hartree–Fock values cited by Pople[1] were derived from 6-31 G* or 4-31 G calculations of energies of molecules, using assumed geometries. We might point out that there seems to be no difficulty in getting reasonably accurate estimates of molecular energies by semiempirical methods if one is willing to make such assumptions. This is illustrated in Table I by a comparison of Pople's results for his 16 reactions with those calculated by MINDO/1.[5] The standard deviations for the nine reactions for which data are available by both methods are 3.22 (HF) and 1.75 (MINDO/1) kcal/mol, respectively. Note that MINDO/1 represented only a preliminary version. We did not pursue this approach further because of the limited scope of a treatment in which geometries are not optimized. With regard to ref 2, it is surprising that no reference is made to calculations of bond lengths. Moreover the major errors he cites again occur in cases to which we have drawn specific attention in our papers.

Table I. Comparison of Errors in Heats of Reaction Calculated by ab Initio SCF and MINDO/1 Methods

Reaction	Error in calcd heat of reaction (kcal/mol) "Hartree–Fock"	MINDO/1
$CH_3CH_3 + H_2 \rightarrow 2CH_4$	−6.4	+0.2
$CH_2{=}CH_2 + 2CH_4 \rightarrow 2CH_3CH_3$	−5.3	−1.6
$HC{\equiv}CH + 4CH_4 \rightarrow 3CH_3CH_3$	−12.1	–
$CH_3CH_2CH_3 + CH_4 \rightarrow 2CH_3CH_3$	−1.2	0.0
$CH_3(CH_2)_2CH_3 + 2CH_4 \rightarrow 3CH_3CH_3$	−4.0	−1.1
$CH_3(CH_2)_3CH_3 + 3CH_4 \rightarrow 4CH_3CH_3$	—	−1.4
$CH_3CH{=}CH_2 + CH_4 \rightarrow CH_3CH_3 + CH_2{=}CH_2$	−1.3	+1.0
$CH_3C{\equiv}CH + CH_4 \rightarrow CH_3CH_3 + HC{\equiv}CH$	0.4	–
$H_2C{=}C{=}CH_2 + CH_4 \rightarrow 2CH_2{=}CH_2$	−1.2	–
$CH_3CH{=}CH_2 \rightarrow \triangle$	0.0	+3.3
$CH_3C{\equiv}CH \rightarrow \triangle$	3.5	–
$CH(CH_3)_3 \rightarrow n\text{-}C_4H_{10}$	1.5	−0.4
$C(CH_3)_4 \rightarrow n\text{-}C_5H_{12}$	–	+1.4
	−1.0	+1.6
 $\rightarrow H_3CC{\equiv}CCH_3$	−2.1	–
$C_6H_6 + 6CH_4 \rightarrow 3CH_3CH_3 + 3CH_2CH_2$	+1.4	+3.0

Since very extensive tests of MINDO/3 have been published,[3] including applications to a wide variety of chemical reactions,[6] there seems no need for further comment.[7]

References and Notes

(1) J. A. Pople, *J. Am. Chem. Soc.*, **97,** 5306 (1975).

(2) W. J. Hehre, *J. Am. Chem. Soc.*, **97,** 5308 (1975).

(3) (a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1285 (1975); (b) *ibid.*, **97,** 1294 (1975); (c) *ibid.*, **97,** 1302 (1975); (d) *ibid.*, **97,** 1307 (1975); (e) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97,** 1311 (1975).

(4) See in particular Figures 2 and 3 of part XXV,[3a] Table I of part XXVI,[3b] Table I of part XXVII,[3c] Table I of part XXVIII,[3d] Table I of part XXIX,[3e] and the discussions on pp 1292,[3a] 1294,[3b] 1302,[3c] 1309–1310,[3d] and 1313.[3e]

(5) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50,** 1262 (1969).

(6) For a review see M. J. S. Dewar, *Chem. Brit.*, **11,** 97, (1975). Most of the work summarized has now been published or is in press.

(7) EDITOR'S NOTE: This communication should have appeared concurrently with the communications cited in ref 1 and 2, but was inadvertently delayed in editorial processing.

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Catalytic Electrochemical Reduction of Acetylene in the Presence of a Molybdenum–Cysteine Complex

Sir:

A chemical model for nitrogenase enzyme[1] based on the binuclear molybdenum(V)-cysteine complex, $Na_2Mo_2O_4(Cys)_2$ (**1**),[2] has been shown to be effective in the catalytic reduction of nitrogenase substrates. A Mo(IV)-cysteine monomer, produced by reduction of **1** with $NaBH_4$ or $Na_2S_2O_4$, has been proposed[1b] as the active species responsible for binding and reducing substrates such as acetylene.