IP of the aromatic increases, an interaction involving at least partial charge transfer from the ketone triplet (as donor) toward the aromatic (as acceptor) is indicated. Interestingly, the reverse type of interaction involving charge transfer to $^3Ph_2CO^*$ from various aliphatic and electron-rich aromatic quenchers has recently been reported,[18] and seems well documented in other cases in quenching of ketone singlets as well as triplets.[19]

Further discussion of these data will be reserved for the full paper. We wish to emphasize, finally, that the time-correlated single photon technique deserves much more attention as a relatively simple and straightforward means of accurate measurement of short triplet lifetimes in solution.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

[18] J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, **94**, 4040 (1972).

[19] See, for example, P. J. Wagner and R. A. Leavitt, *ibid.*, **92**, 5806 (1970); I. E. Kochevar and P. J. Wagner, *ibid.*, **94**, 3859 (1972); N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971); R. R. Hautala and N. J. Turro, *ibid.*, **93**, 5595 (1971).

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Ab Initio Molecular Orbital Studies of Cyclic Nitric Oxide Dimer

Sir:

Recently Williams and Murrell[1] published a nonempirical SCF–MO study of the nitric oxide dimer using a minimum basis of Slater atomic orbitals. They found that the trans conformation is the most stable in the gas phase with the cis conformation having an energy 3.5 kcal/mol higher. These findings are in disagreement with the vibrational spectra of pure solid NO,[2] of the matrix-isolated NO clusters,[2b,3] and of liquid[2a] and gaseous NO[4] which indicate that the most stable form of $(NO)_2$ is noncentrosymmetric. In this laboratory we have studied the NO dimer as a possible intermediate in nitrate ester combustion. The results of our minimum basis *ab initio* SCF calculations indicate that the cyclic isomer is the most stable.

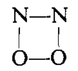
Our investigation of $(NO)_2$ was conducted using POLYATOM,[5] a Gaussian system of SCF programs kindly supplied by Professor Moskowitz. To obtain results of single ζ quality, we employed the 7,3 Gaussian atomic basis functions proposed by Whitman and Hornback.[6] These functions were contracted to two s and one p type function on each center. For the purposes of comparison we repeated the calculations of Williams and Murrell[1] using our basis set. The energy of the trans conformation was found to be −257.59643 au. However, the energy of the cis conformation suggested by these authors[1] was calculated to be −257.60110 au which is lower than the value for the trans isomer. These data are presented in Table I.

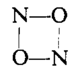
Table I. Calculated Geometries and Energies of $(NO)_2$[a]

Structure	R(NN)	∠NNO	R(NO)	Energy rel to trans
Cis	(1.57)	(110.2)	(1.23)	−2.9 (3.5)
Trans	(1.53)	(104.6)	(1.23)	0.0 (0.0)
Cyclic (I)	1.35	93.0	1.51	−8.8

[a] Bond length in ångströms, angles in degrees, and energies in kilocalories per mole. Values in parentheses are from ref 1.

We next considered the cyclic structures I and II for


I


II

the NO dimer. Structure II was studied by restricting it to a planar-square configuration. A minimum energy of −257.51855 au was obtained at an ON bond length of 1.35 Å. Since this energy is somewhat above the lowest energy computed by Williams and Murrell,[1] structure II was not considered further. Structure I was also restricted to the square-planar conformation and the energy computed as a function of bond length. A minimum was obtained at a bond distance of 1.46 Å, the energy being −257.59595 au. This structure is quite competitive with the trans structure proposed in ref 1. To obtain a more realistic minimum, the "square" restriction was relaxed. A minimum energy of −257.61053 au was thus obtained. This energy corresponds to R(NN) = 1.35 Å and R(NO) = R(OO) = 1.51 Å. The energy minimization was carried out on a rather coarse grid of 0.05 Å so that the error in the above bond lengths should be plus or minus 0.05 Å. Structure I is thus about 8.8 kcal/mol more stable than the trans structure of Williams and Murrell[1] as can be seen in Table I.

Our calculations disagree with those of Williams and Murrell[1] on two points. We find that the cyclic isomer has the lowest energy and that the cis structure is 2.9 kcal/mol below, rather than 3.5 kcal/mol above, the trans. The first discrepancy may have occurred simply because Williams and Murrell[1] did not consider structures of type I. The second discrepancy is probably due to some loss of accuracy in the multicenter two-electron integrals. Guest, *et al.*,[7] have compared calculations of the type employed in ref 1 with more accurate calculations in the literature using the same basis set. Errors as large as 0.05 au in the case of ozone were found. These errors probably tend to cancel when similar geometries are compared. However, the cis and trans structures of ONNO seem to be sufficiently different so that the errors do not quite cancel and a discrepancy of several kilocalories per mole can occur.

The results of our calculations are in agreement with

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[1] J. E. Williams and J. N. Murrell, *J. Amer. Chem. Soc.*, **93**, 7149 (1971).

[2] (a) A. L. Smith, W. E. Keller, and H. L. Johnston, *J. Chem. Phys.*, **19**, 189 (1951); (b) W. G. Fateley, H. A. Bent, and B. Crawford, *ibid.*, **31**, 204 (1959).

[3] W. A. Guillory and C. E. Hunter, *ibid.*, **50**, 3516 (1969).

[4] C. E. Dinerman and G. E. Ewing, *ibid.*, **53**, 626 (1970).

[5] I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta*, **6**, 191 (1966).

[6] D. R. Whitman and C. J. Hornback, *J. Chem. Phys.*, **51**, 398 (1969).

[7] M. F. Guest, J. N. Murrell, and J. B. Pedley, *J. Mol. Phys.*, **20**, 81 (1971).

experiment since they predict that the most abundant form of $(NO)_2$ is noncentrosymmetric. However, they cannot be taken as the final word on the structure of the dimer. Our calculated geometry does not agree very well with the analysis performed by Dinerman and Ewing[4] on the unresolved P, Q, and R structure of $(NO)_2$. The equilibrium bond lengths in our calculation for structure I are more indicative of N–O single bonds whereas the observed stretching frequencies are characteristic of NO double bonds. Possibly an improved calculation would give better agreement with experiment. We present our work simply to encourage investigators to consider cyclic $(NO)_2$ in their interpretation of future theoretical and experimental work.

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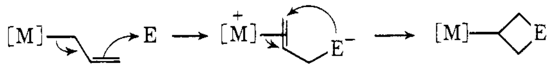
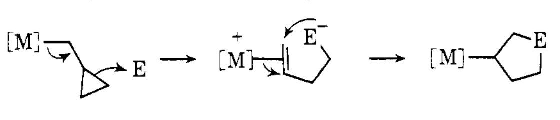
Synthesis of γ-Lactams and Sultams by Metal Assisted Cycloaddition. Stereochemistry of Cycloaddition and of the Deprotonation of Cationic *Pentahapto*cyclopentadienyldicarbonyl(olefin)iron Complexes

Sir:

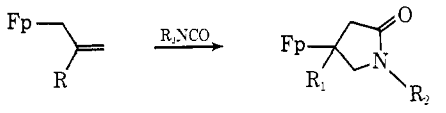
We recently showed that the reactions of h^1-allyliron and of cyclopropylmethyliron complexes with electrophilic olefins and with SO_2 gave cycloaddition products whose formation was accounted for in terms of a two-step reaction sequence involving the initial formation of homologous dipolar intermediates and their subsequent closure[1,2] (eq 1 and 2). We now wish to report


(1)


(2)

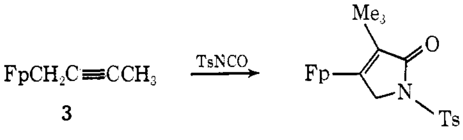
the extension of these cycloaddition reactions to isocyanates, which provides a new and expeditious route to γ-lactams from cyclic and acyclic allyl and propargyliron complexes.[2a]

Although the allyliron complex **1a** does not react with either ethyl or phenyl isocyanate, 2,5-dichlorophenyl isocyanate reacts over a period of several days at room temperature to give the butyrolactam (**2a**),[3] mp 153–155°, in moderate yield. With the highly reactive chlorosulfonyl isocyanate, **1a** reacts instantaneously below 0° affording the chlorosulfonyl lactam (**2b**): ir (CH_2Cl_2) 1767 (C=O), 1967, 2014 cm^{-1} (C≡O). This substance may be converted in 72% overall yield to the unsubstituted lactam **2c**,[3] dec 180–181° (ir (KBr) 1675 (C=O), 1940, 1995 cm^{-1} (C≡O)), by treatment with thiophenol in the presence of sodium methoxide.[4] Toluenesulfonyl and methoxysulfonyl[5] isocyanates react similarly, within 30 min at room temperature, with **1a** and the methallyl complex **1b** to give the butyrolactams (**2d–f**)[3] in 40–70% yield. The butynyl complex **3** also reacts with toluenesulfonyl isocyanate affording the butenolactam (**4**[3]: ir (KBr) 1695 (C=O) 1960, 2020 cm^{-1} (C≡O); nmr (CD_3NO_2) τ 4.88 (s, 5, Cp), 5.59 (q, 2, J = 1.5 Hz, CH_2), 7.58 (s, 3, $ArCH_3$), 8.20 (t, 3, J = 1.5 Hz, CH_3C=).



1a, R = H
b, R = Me

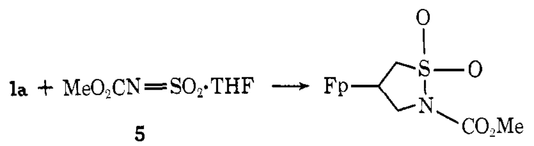
2a, $R_1 = H$; $R_2 = 2,5\text{-}Cl_2C_6H_5$
b, $R_1 = H$; $R_2 = SO_2Cl$
c, $R_1 = H$; $R_2 = H$
d, $R_1 = H$; $R_2 = Ts$
e, $R_1 = Me$; $R_2 = Ts$
f, $R_1 = H$; $R_2 = MeOSO_2$



3 **4**

Fp ≡ $h^5\text{-}C_5H_5Fe(CO_2)$

Finally, the *N*-sulfonylurethane (**5**), derived by treatment of carbomethoxysulfamoyl chloride with sodium hydride following the recently reported procedure of Burgess and Williams,[6] has also been found to enter into a (2 + 3) cycloaddition reaction to give the γ-sultam (**6**): (KBr) 1940, 1995 (C≡O), 1695 (C=O), 1300, 1145 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 4.96 (s, 5, Cp), 6.06 (s, 3, Me), 6.0–7.2 (m, 5, CH,CH_2).



5 **6**

Extension of these reactions to cycloalkenyliron complexes provides a means for examining the stereospecificity of the cycloaddition process. The requisite 3-cyclopentenyl- and 3-cyclohexenyliron complexes (**7**) may be prepared by deprotonation of the related

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[1] W. P. Giering and M. Rosemblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971).

[2] Similar reactions of **1** and of the related molybdenum complex with tetracyanoethylene have recently been reported by S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, **31**, C34 (1971). We have also found that h^1-allyl derivatives of cyclopentadienyltungsten tricarbonyl, cyclopentadienylchromium dinitrosyl, and cobaloxime also give cycloaddition products with TCNE, and that β,β-dicyano-*o*-chlorostyrene likewise enters into cycloaddition reactions with h^1-allylmetal complexes.

[2a] Note Added in Proof. Since submitting this paper, a paper by Y. Yamamoto and A. Wojcicki, *Inorg. Nucl. Chem. Lett.*, 883 (1972), has appeared reporting similar results.

[3] An acceptable elemental analysis was obtained for this substance and its ir and nmr spectra were compatible with the structure assigned.

[4] R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963); *Org. Syn.*, **46**, 51 (1966).

[5] R. Graf, *Chem. Ber.*, **96**, 56 (1963); R. Lattrell and G. Lohaus, German Patent No. 1,300,556 (1969); *Chem. Abstr.*, **71**, 101292 (1969).

[6] E. M. Burgess and W. M. Williams, *J. Amer. Chem. Soc.*, **94**, 4386 (1972).