

are based on the displacements of LMO centroids of charge during the reaction and thus theoretical support is given to one set of bond reorganizations or "electron pushing". A comparison of the bond reorganizations for the azidoazomethine and vinyl azide cyclizations demonstrates the importance of the terminal lone pair in forming a new bond with a subsequent rearrangement of the π system for the former case. In the case of vinyl azide and protonated azidoazomethine the π system must be disrupted in order to participate directly in the formation of a new bond.

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A Theoretical Study of Substituted CHNO Isomers

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Abstract: A detailed ab initio molecular orbital study using minimal and split-valence basis sets has been carried out for singlet isomers of R(CNO), R = Li, BH₂, CH₃, NH₂, OH, F, Cl, CN, C₆H₅, *p*-NH₂C₆H₄, and *p*-NO₂C₆H₄. Calculated structures are in reasonable agreement with available experimental data. The predicted equilibrium structures generally resemble those of the parent compounds (R = H). Only the lithium substituent leads to large structural distortions: LiNCO, LiOCN, and LiONC are all predicted to be linear molecules. Methyl fulminate (CH₃ONC) is predicted to be quite stable toward intramolecular rearrangement and of comparable thermodynamic stability to acetonitrile oxide (CH₃CNO). There is no theoretical evidence that any of the substituted oxazirines $\overline{\text{RCNO}}$ are kinetically stable compounds. The calculations suggest that hydroxycarbonyl- and fluorocarbonylnitrene are low-energy isomers but with relatively small barriers toward intramolecular rearrangement. Other substituted singlet carbonyl nitrenes (R = Li, CH₃, Cl) rearrange without activation to the corresponding isocyanate.

Introduction

In a previous paper,² we presented an ab initio molecular orbital study of the isomers of CHNO and the reaction pathways which interconnect them. We found that the most stable isomer is HNCO (isocyanic acid) followed by HOCN (cyanic acid), HCNO (formonitrile oxide), and HONC (carboxime). Detailed investigation of the CHNO potential surface suggested that, in addition to the two experimentally characterized molecules isocyanic acid and formonitrile oxide, two additional isomers, namely, cyanic acid and carboxime, are likely to be reasonably stable species and should be observable under suitable conditions. Other conceivable CHNO isomers such as singlet formyl nitrene and oxazirine were found to collapse with little or no activation to more stable structures. From a structural point of view, an important result was that HNCO, HOCN, and HONC are all predicted to be trans-bent molecules. This result has been confirmed in other independent calculations.³

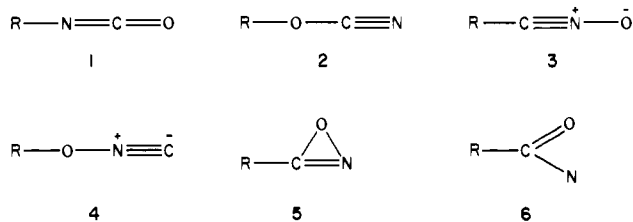
The main objective of the present work is to determine theoretically the effect of substituents on the structures and stabilities of CHNO isomers and, in particular, on the stabilities of the lesser known isomers, viz., fulminates (RONC), oxazirines ($\overline{\text{RC=N-O}}$), and carbonylnitrenes (RC(O)N). For the latter class of compounds, there is some experimental information against which the theoretical results may be judged.

Methods and Results

Two Gaussian-type basis sets were used in this study. The simpler of these, the minimal STO-3G set,⁴ was employed for geometry optimizations and direct calculations of transition states using procedures described previously.⁵ The transition states are characterized as stationary points in the surface with one negative eigenvalue of the energy second derivative matrix. Single calculations at STO-3G optimized geometries were then carried out using the split-valence 4-31G basis set.⁶ Finally,

structures of special interest were reoptimized at the 4-31G level. All calculations desired in this paper are of the single determinant Hartree-Fock type⁷ and were carried out with a modified version of the Gaussian 70 series of programs.⁸

The RCNO isomers considered in the present work are isocyanates (1), cyanates (2), nitrile oxides (3), fulminates (4), oxazirines (5), and carbonylnitrenes (6) with R = H, Li, BH₂,



CH₃, NH₂, OH, F, Cl, CN, C₆H₅, *p*-NO₂C₆H₄, and *p*-NH₂C₆H₄. In view of the large number of possible isomers, full geometry optimization was not always attempted. In an initial series of calculations, we employed a partially optimized model geometry, which is based on standard parameters⁹ for the internal geometry of the substituent, linked to CNO fragment structures taken from calculations for R = H. The remaining two geometric parameters, one bond length and one bond angle (e.g., $r(\text{R}-\text{N})$ and $\theta(\text{RNC})$ in (1)) were optimized, in some cases for several values (corresponding to different conformations) of a third parameter, a dihedral angle. To reduce the number of possible conformers, the slight nonlinearity of the CNO chains in 1, 2, and 4 (R = H) was neglected, i.e., the geometry of the CNO chain was taken from optimum structures of CHNO isomers in which the CNO moiety was constrained to be linear. Resulting geometries and energies are collected in Table I.

In a second series of calculations full optimization at the STO-3G level was carried out for molecules which are either experimentally known or bear a close relationship to experimentally known systems (R = CH₃, OH, Cl), and, in addition, for substituents which could be expected to exert a marked influence upon the structure of the CNO fragment (R = Li, F, CN). The resulting energies are shown in Table II; the optimum geometries are specified in structural diagrams during the course of the paper. Unless noted otherwise, all structural parameters discussed in the following are STO-3G values, whereas relative energies are 4-31G values for optimum STO-3G geometries. Bond lengths are given in ångströms, bond angles in degrees.

Nomenclature

The choice of nomenclature for the molecules studied in this paper is not clear-cut. We have used the following system, which is straightforward and unambiguous and conforms in most respects with accepted IUPAC rules.⁹ Molecules RNCO, ROCN, and RONC are named as isocyanates, cyanates, and fulminates, respectively. This is the obvious thing to do for molecules such as CH₃NCO (methyl isocyanate) and PhNCO (phenyl isocyanate). We have used this method also in the less obvious cases, e.g., FCNO (fluorine isocyanate), HONCO (hydroxyl isocyanate), NH₂NCO (aminyl isocyanate), and NCNCO (cyanogen isocyanate). Molecules RCNO have been named as substituted formonitrile oxides, e.g., NH₂CNO (aminofornitrile oxide), FCNO (fluorofornitrile oxide), except where common names appeared more appropriate, e.g., CH₃CNO (acetonitrile oxide), PhCNO (benzonitrile oxide). We have named the molecules RC(O)N as carbonyl nitrenes, e.g., HOC(O)N (hydroxycarbonylnitrene), FC(O)N (fluorocarbonylnitrene), again with exceptions where common names are already in use, e.g., PhC(O)N (benzoylnitrene).

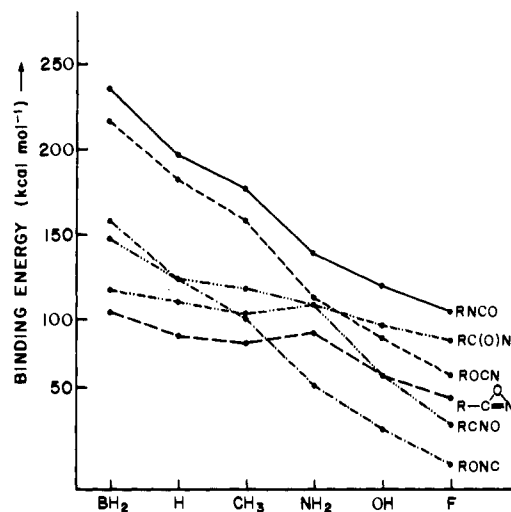


Figure 1. Theoretical binding energies for RCNO isomers.

Finally, the systems $\overline{\text{RCNO}}$ are named, using standard substitutive nomenclature, as substituted oxazirines.

Discussion

We begin by making some general observations after which we examine results for each substituent in turn. As an aid to understanding the effect of substituents on relative energies of RCNO isomers, it is convenient to consider initially the theoretical binding energies E_b , e.g., $E_b(\text{FCNO}) = E(\text{FCNO}) - E(\text{F} + \text{C} + \text{N} + \text{O})$. Some of these values which have been derived from data in Tables I and II¹¹ are displayed in Figure 1. We note that relative binding energies for a given substituent are identical with the relative energies in Table I or II. The point of calculating the binding energies is to establish a common reference point from which stabilizing or destabilizing effects of substituents can be assessed. We caution against placing too much faith in the *absolute* values of the binding energies.

Examination of Figure 1 shows that the binding energy curves for ROCN and RONC are almost identical, i.e., the effects of substituents in the two systems are very similar as might have been anticipated. The RNCO curve also follows a similar path. On the other hand, the RCNO, $\overline{\text{RC}}=\text{N}-\text{O}$, and RC(O)N curves follow quite different paths. The results may be rationalized in terms of relative bond energies. For example, the apparent stabilization of the formonitrile oxide, formyl-nitrene, and oxazirine molecules by a hydroxy substituent reflects in part the weakness of the N-O and O-O single bonds in the other isomers HONCO, HOOCN, and HOONC. Again, the low relative energy of aminofornitrile oxide is not so much due to a special stabilization of the H₂NCNO structure than to the weakness of the N-N bond in aminyl isocyanate. As expected on the basis of average bond energies, the ROCN and RONC structures are destabilized (relative to RNCO) by amino, hydroxy, and fluoro substituents. We may also note at this point that none of the substituents that we have examined stabilizes the carboxime molecule (relative to HNCO).

If bond energies were additive and independent of the chemical environment, the relative energy of nitrile oxides, carbonylnitrenes, and oxazirines should not depend on the substituent. However, we find that, whereas formonitrile oxide is more stable than formyl-nitrene, FCNO is of higher energy than fluorocarbonylnitrene (cf. Table II). A convenient framework for the discussion of effects of this nature is provided by isodesmic¹² stabilization reactions of the type



Table I. Partially Optimized Structures and Energies of RCNO Isomers^a

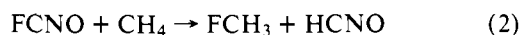
R	RXYZ	Geometry		Total energy		Rel energy 4-31G
		r(R-X)	θ(RXY)	STO-3G	4-31G	
H	HNCO	1.037	112.5	-165.500 50	-167.482 91	0.0
	HOCN	0.993	104.9	-165.511 76	-167.457 30	16.1
	HCNO	1.065	180.0	-165.392 21	-167.367 59	72.4
	HONC	1.001	101.6	-165.440 98	-167.364 74	74.2
	HC(O)N	1.122	105.4	-165.391 46	-167.345 19	86.4
	$\overline{\text{HCNO}}$	1.083	150.9	-165.406 29	-167.312 03	107.2
Li	LiNCO	1.601	180.0	-172.344 34	-174.418 84	0.0
	LiOCN	1.477	180.0	-172.337 19	-174.403 94	9.4
	LiCNO	1.824	180.0	-172.193 88	-174.282 32	85.7
	LiONC	1.463	180.0	-172.254 61	-174.296 26	76.9
	LiC(O)N	2.445	43.9	-172.229 29	-174.287 93	82.1
	$\overline{\text{LiCNO}}$	1.907	138.5	-172.174 61	-174.207 49	132.6
BH ₂ (planar)	H ₂ BNCO	1.399	144.9	-190.502 83	-192.747 68	1.7
	H ₂ BOCN	1.363	119.0	-190.520 45	-192.719 60	19.3
	H ₂ BCNO	1.492	180.0	-190.376 33	-192.608 89	88.8
	H ₂ BONC	1.370	114.3	-190.447 19	-192.626 13	78.0
	H ₂ BC(O)N	1.610	102.8	-190.339 48	-192.561 16	118.7
	$\overline{\text{H}_2\text{BCNO}}$	1.548	148.5	-190.369 99	-192.540 42	131.8
BH ₂ (perp)	H ₂ BNCO	1.382	180.0	-190.502 03	-192.750 39	0.0
	H ₂ BOCN	1.399	118.8	-190.495 23	-192.702 63	30.0
	H ₂ BONC	1.445	97.8	-190.415 81	-192.599 46	94.7
	H ₂ BC(O)N	1.621	107.7	-190.335 03	-192.558 33	120.5
	$\overline{\text{H}_2\text{BCNO}}$	1.555	151.8	-190.368 44	-192.540 16	131.9
	H ₃ CNCO	1.491	121.0	-204.079 98	-206.453 77	0.0
CH ₃	H ₃ COCN	1.454	110.1	-204.093 58	-206.426 08	17.4
	H ₃ CCNO	1.484	180.0	-203.988 56	-206.363 51	56.6
	H ₃ CONC	1.459	106.6	-204.026 31	-206.336 41	73.6
	H ₃ CC(O)N ^b	1.556	105.5	-203.938 43	-206.338 31	72.5
	$\overline{\text{H}_3\text{CCNO}}$ ^b	1.504	151.2	-204.004 13	-206.310 82	89.7
	H ₂ NNCO	1.422	117.9	-219.768 30	-222.364 31	0.0
NH ₂ (planar)	H ₂ NOCN	1.426	107.8	-219.764 66	-222.312 09	32.8
	H ₂ NCNO	1.356	180.0	-219.704 95	-222.318 02	29.0
	H ₂ NONC	1.432	105.0	-219.698 46	-222.222 75	88.8
	H ₂ NC(O)N	1.415	106.6	-219.716 84	-222.317 19	29.6
	$\overline{\text{H}_2\text{NCNO}}$	1.357	152.6	-219.738 84	-222.288 77	47.4
	H ₂ NNCO	1.439	115.6	-219.763 51	-222.362 91	0.9
NH ₂ (perp)	H ₂ NOCN	1.400	109.1	-219.774 85	-222.323 33	25.7
	H ₂ NONC	1.389	108.5	-219.714 90	-222.240 39	77.8
	H ₂ NC(O)N	1.438	95.8	-219.707 83	-222.311 05	33.4
	$\overline{\text{H}_2\text{NCNO}}$	1.384	151.8	-219.721 88	-222.268 15	60.3
	HONCO	1.424	112.5	-239.297 40	-242.149 15	0.0
	HOOCN	1.408	104.4	-239.296 40	-242.097 01	32.7
OH (planar) ^c	HOCNO	1.353	167.3	-239.217 74	-242.085 31	40.1
	HOONC	1.383	102.9	-239.237 55	-242.008 72	88.1
	HOC(O)N ^d	1.389	105.5	-239.245 50	-242.113 57	22.3
	$\overline{\text{HOCNO}}$	1.344	149.5	-239.254 09	-242.061 38	55.1
	HONCO	1.431	114.1	-239.291 29	-242.142 96	3.9
	HOOCN	1.401	107.5	-239.299 67	-242.096 86	32.8
OH (perp)	HOONC	1.397	106.0	-239.240 10	-242.012 44	85.8
	HOC(O)N	1.411	104.7	-239.234 32	-242.100 20	30.7
	$\overline{\text{HOCNO}}$	1.358	151.9	-239.246 38	-242.052 22	60.8
	FNCO	1.393	112.8	-262.908 06	-266.103 90	0.0
	FOCN	1.366	106.4	-262.908 35	-266.044 27	37.4
	FCNO	1.325	180.0	-262.825 49	-266.039 31	40.5
F	FONC	1.362	104.6	-262.848 11	-265.960 83	89.8
	FC(O)N	1.361	107.4	-262.858 57	-266.078 91	15.7
	$\overline{\text{FCNO}}$	1.317	151.7	-262.863 93	-266.017 72	54.1
	CINCO	1.799	108.7	-619.468 18	-266.822 56	0.0
	CIOCN	1.748	108.5	-619.459 88	-266.785 90	23.0
	CICNO	1.698	180.0	-619.373 41	-266.743 11	49.9
Cl	CIONC	1.753	107.5	-619.394 60	-266.697 91	78.2
	CIC(O)N	1.819	102.6	-619.405 82	-266.751 15	44.8
	$\overline{\text{CICNO}}$	1.727	150.3	-619.400 84	-266.698 11	78.1
	CNCO	1.381	123.5	-256.040 71	-259.041 34	0.0
	NCOCN	1.369	111.4	-256.033 11	-258.981 52	37.5
	NCCNO	1.392	180.0	-255.941 56	-258.941 92	62.4
CN	NCONC	1.381	107.6	-255.962 13	-258.887 52	96.5
	NCC(O)N	1.504	105.4	-255.932 01	-258.913 96	79.9

Table I (Continued)

R	RXYZ	Geometry		Total energy		Rel energy 4-31G
		r(R-X)	θ(RXY)	STO-3G	4-31G	
C ₆ H ₅ ^e	NCCNO	1.432	150.1	-255.949 39	-258.882 21	99.9
	C ₆ H ₅ NCO	1.447	125.1	-392.260 06		0.0
	C ₆ H ₅ OCN	1.425	115.4	-392.269 11		17.4
	C ₆ H ₅ CNO	1.454	180.0	-392.164 58		64.4
	C ₆ H ₅ ONC	1.438	112.3	-392.198 64		75.4
	C ₆ H ₅ C(O)N	1.535	107.7	-392.153 53		84.8
p-NH ₂ C ₆ H ₄ ^{e,f}	RNCO	(1.447)	(125.1)	-446.574 20		0.0
	ROCn	(1.425)	(115.4)	-446.583 47		17.3
	RCNO	(1.454)	(180.0)	-446.481 96		62.3
	RONC	(1.438)	(112.3)	-446.513 00		75.3
p-NO ₂ C ₆ H ₄ ^{e,f}	RNCO	(1.447)	(125.1)	-592.951 97		0.0
	ROCn	(1.425)	(115.4)	-592.958 97		18.7
	RCNO	(1.454)	(180.0)	-592.852 91		66.6
	RONC	(1.438)	(112.3)	-592.888 58		76.6

^a Bond lengths in Å, bond angles in degrees, total energies in hartrees, relative energies in kcal mol⁻¹. For carbonylnitrenes and oxazirines, Y = N. ^b HCXY trans. ^c HOXY cis. ^d HOXY cis. ^e Relative "pseudo-4-31G" values derived from STO-3G data for isodesmic processes HNCN + R(CNO) → RNCN + H(CNO) and 4-31G data for relative energies of HNCN and H(CNO). ^f r(R-X) and θ(RXY) assumed to be the same as in the unsubstituted phenyl derivatives.

For example, the energy change in the reaction

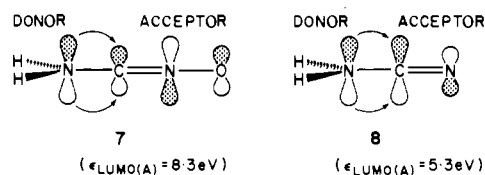


$$\Delta E = -29 \text{ kcal mol}^{-1}$$

is negative and indicates a relative destabilizing interaction between the fluorine substituent and the CNO fragment. Stabilization energies obtained in this manner are listed in Table III.

We may note the following.

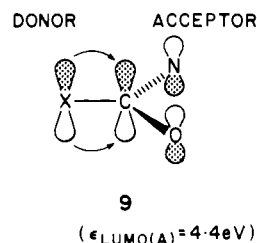
(1) The nitrile oxide fragment is both a σ and a π acceptor and can thus be stabilized by π donors (e.g., **7**) and by σ donors, but will be destabilized by σ acceptors. The π -donor ability decreases in the order NH₂ > OH > F and the σ -acceptor strength increases in the order NH₂ < OH < F. A combination of stabilizing π -donation and destabilizing σ -acceptance by the substituent leads to the calculated decrease of stabilization energies in the order NH₂ > OH > F. The moderate stabilization by a methyl group can be ascribed to a combination of π (hyperconjugative)- and σ -donation. Note that the lowest unoccupied molecular orbital (LUMO) of a nitrile oxide group (cf. **7**) is of higher energy^{13,14} than the LUMO of a cyano group (cf. **8**) and is less concentrated at carbon. Its π -acceptor



properties are therefore less pronounced. As a consequence the σ -electron destabilization becomes more important in the nitrile oxides leading to lower (or more negative) stabilization energies compared with corresponding nitriles¹⁵ for electronegative substituents.

(2) The carbonyl group is a strong π acceptor and the stabilization energies in carbonylnitrenes can be rationalized in terms of the capability of substituents to donate electrons into the antibonding π orbital (cf. **9**). Thus the stabilization varies in the sequence CH₃ < NH₂ > OH > F.

(3) The oxazirine ring ($\epsilon_{\text{LUMO}} = 6.8 \text{ eV}$) is a stronger π acceptor than the nitrile oxide but a weaker π acceptor than the carbonylnitrene. The hybridization of the carbon atom in oxazirine is intermediate between formonitrile oxide and formylnitrene. This effect, which can also be held responsible for the variation of R-C bond lengths in nitrile oxides, oxa-



zirines, and carbonylnitrenes, leads to a σ -acceptor strength of the oxazirine fragment which is intermediate between that of the nitrile oxide and formylnitrene fragments. As a result, the oxazirine isomer is destabilized relative to the nitrene by electronegative substituents. The stabilization energies decrease in the order NH₂ > OH > F for both the oxazirines and nitrenes but the decrease occurs at a faster rate in the oxazirines because of the extra σ -destabilization.

In summary, we can interpret the more dramatic substituent effects as follows. The high relative stability of aminoformonitrile oxide may be attributed largely to the strength of the C-N single bond (in H₂NCNO) compared with the N-N and N-O bonds in the isomeric molecules H₂NNCO, H₂NOCN, and H₂NONC. The high relative stability of hydroxycarbonylnitrene and fluorocarbonylnitrene can be ascribed to the weakness of N-F and O-F bonds in the corresponding isocyanates, cyanates, and fulminates, and to the destabilization of the nitrile oxides HOCNO and FCNO by the strong σ -acceptors OH and F. The high relative stability of aminooxazirine may be attributed to the strength of the C-N single bond and to the strong π -acceptor and weak σ -acceptor properties of the oxazirine ring.

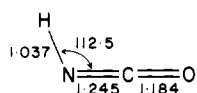
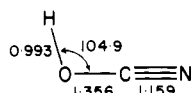
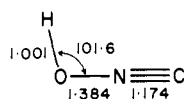
We now turn to a detailed discussion of our results for the individual isomers and their relationship with available experimental data.

R = H. The unsubstituted RCNO isomers have been discussed in detail elsewhere.² At this point, we only note that the results obtained with the assumption of a linear (CNO) fragment (**10-13**) do not differ significantly from the fully optimized structures (**14-17**).

R = Li. In contrast to the parent (R = H) compounds, lithium isocyanate (**20**), lithium cyanate (**21**), and lithium fulminate (**23**) prefer linear geometries in which the delocalization of the nitrogen and oxygen lone pairs into the empty 2p orbitals on lithium is maximized. Simple electronegativity arguments would suggest that the Li-X bond strength increases in the order C < N < O. The extended basis set cal-

Table II. Total and Relative Energies of RCNO Isomers (Full STO-3G Optimization)

Molecule	Structure no.	Total energy, hartrees		Rel energy, kcal mol ⁻¹
		STO-3G	4-31G	
HNCO	14	-165.502 92	-167.484 70	0.0
HOCN	15	-165.511 98	-167.457 39	17.1
HCNO	16	-165.392 21	-167.367 59	73.5
HONC	17	-165.441 45	-167.365 45	74.8
HC(O)N	18	-165.391 46	-167.345 19	87.5
HCNO	19	-165.406 29	-167.312 03	108.4
LiNCO	20	-172.325 91	-174.423 77	0.0
LiOCN	21	-172.340 04	-174.411 39	7.8
LiCNO	22	-172.194 97	-174.277 21	92.0
LiONC	23	-172.256 33	-174.300 41	77.4
LiCNO	24	-172.177 21	-174.200 90	139.9
CH ₃ NCO	31	-204.083 29	-206.457 72	0.0
CH ₃ OCN	32	-204.094 51	-206.426 72	19.5
CH ₃ CNO	33	-203.988 75	-206.363 18	59.3
CH ₃ ONC	34	-204.027 41	-206.337 55	75.4
CH ₃ C(O)N	35	-203.983 72	-206.340 94	73.3
CH ₃ C(O)N	36	-203.983 23	-206.339 09	74.4
CH ₃ CNO	37	-204.004 20	-206.310 14	92.6
CH ₃ CNO	37a	-204.004 98	-206.311 85	91.5
HONCO	48	-239.306 59	-242.147 72	0.0
HONCO	49	-239.292 08	-242.130 61	10.7
HOOCN	51	-239.304 29	-242.097 44	31.6
HOOCN	52	-239.292 69	-242.083 73	40.2
HOOCN	53	-239.304 29	-242.096 78	32.0
HOCNO	54	-239.222 06	-242.063 94	52.6
HOONC	56	-239.240 34	-242.009 29	86.9
HOONC	57	-239.232 82	-242.002 57	91.1
HOONC	58	-239.243 01	-242.010 96	85.8
HOC(O)N	59	-239.248 14	-242.108 64	24.5
HOC(O)N	60	-239.239 92	-242.093 75	33.9
HOCNO	63	-239.256 58	-242.061 94	53.8
HOCNO	64	-239.256 21	-242.059 10	55.6
FNCO	65	-262.912 23	-266.103 17	0.0
FOCN	66	-262.908 90	-266.042 58	38.0
FCNO	67	-262.829 93	-265.997 94	66.0
FCNO	67a	-262.826 01	-266.038 59	40.5
FCNO (triplet)	69	-262.908 30		
FONC	70	-262.848 33	-265.960 21	89.7
FC(O)N	71	-262.859 44	-266.076 46	16.8
FCNO	72	-262.864 84	-266.022 45	50.7
ClNCO	75	-619.471 74	-625.823 67	0.0
ClOCN	76	-619.460 25	-625.784 68	24.5
ClCNO	77	-619.373 45	-625.742 55	50.9
ClONC	78	-619.395 03	-625.698 22	78.7
ClCNO	80	-619.401 02	-625.700 30	77.1
NCNCO	81	-256.044 06	-259.042 45	0.0
NCOCN	82	-256.033 92	-258.981 01	38.6
NCCNO	83	-255.942 11	-258.942 12	63.0
NCONC	84	-255.962 92	-258.890 87	95.1
NCC(O)N	85	-255.932 19	-258.912 68	81.4
NCCNO	86	-255.949 59	-258.880 18	101.8

10
(C_s)11
(C_s)12
(C_{2v})13
(C_s)

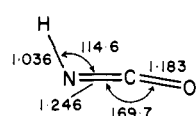
culations indicate that this effect is not sufficient to reverse the relative energy of the isocyanate and cyanate structures, although the energy difference is reduced from 17 (R = H) to 8 (R = Li) kcal mol⁻¹. However, lithium *is* predicted to bind preferentially to the more electronegative end of the fulminate anion, the fulminate **23** being more stable than the nitrile oxide **22** by 15 kcal mol⁻¹. Partial optimization (Table I) of the lithiated formylnitrene **25** leads to a structure with lithium bridging the C-N single bond; upon full optimization, **25** collapses to **20**. The cyclic isomer **24** is 140 kcal mol⁻¹ less stable than lithium isocyanate.

CNDO/2 calculations on LiNCO and LiOCN have been reported by Rode et al.,¹⁶ who find that LiNCO is bent and of

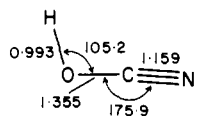
Table III. Stabilization Energies (kcal mol⁻¹) for selected RCNO Isomers^a

R	Stabilization energy		
	R-CNO	R-C(O)N	R-C≡N ⁺ O ⁻
CH ₃	12.3	12.4	14.9
NH ₂	15.8	29.4	32.3
OH	-19.5	22.6	14.1
F	-28.9 ^b	8.9	-4.2

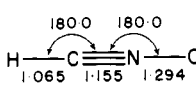
^a Calculated as energy changes in reaction 1 using data in Tables I (R = NH₂) and II (R = H, CH₃, OH, F) and 4-31G energies for STO-3G optimized structures from ref 32 for CH₄ (-40.139 76), C₂H₆ (-79.115 82), CH₃NH₂ (-95.064 98), CH₃OH (-114.867 16), and CH₃F (-138.856 86). ^b Calculated for structure 67a.



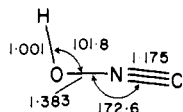
14
(C_i → C_s)



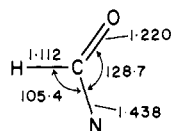
15
(C_i → C_s)



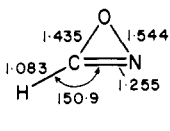
16
(C_i → C_{2v})



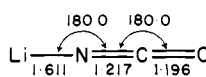
17
(C_i → C_s)



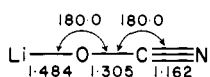
18
(C_i → C_s)



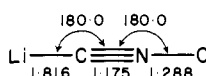
19
(C_i → C_s)



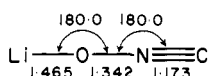
20
(C_s → C_{2v})



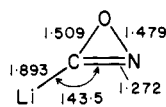
21
(C_s → C_{2v})



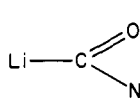
22
(C_s → C_{2v})



23
(C_s → C_{2v})



24
(C_i → C_s)

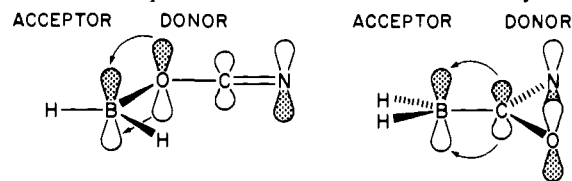


25

lower energy than LiOCN. A compound with the empirical formula LiNCO has been prepared,¹⁷ but its structure is unknown.

R = BH₂. The BH₂ substituent was examined using a planar model geometry, leading to two possible conformations in which the BH₂ groups are respectively planar and perpendic-

ular with respect to the part of the molecule to which they are attached. The tendency of H₂BOCN, H₂BONC, H₂BC(O)N, and H₂BCNO to adopt planar conformations can be understood on the basis of simple orbital interaction diagrams, e.g., 26 and 27. The planar conformation is stabilized by the in-

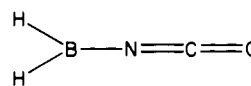


26

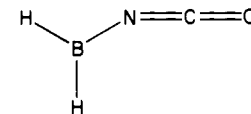
27

teraction of the CNO fragment HOMO and the empty p orbital (LUMO) on the BH₂ substituent. Since the highest occupied orbitals of the nitrene and oxazirine fragments have their greatest amplitude at the nitrogen atom (cf. 27), this extra stabilization is smaller and the energy difference between planar and perpendicular conformations is smaller than in the case of H₂BOCN and H₂BONC.

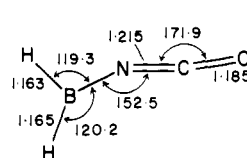
The most stable BH₂-substituted isomer is H₂BNCO. Since bending the BNC angle requires little energy (the energy difference between the partially optimized structures 28 and 29 is less than 2 kcal mol⁻¹), a full geometry optimization was



28

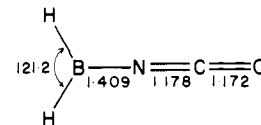


29



30

(C_s, STO-3G,
E = -190.50613)

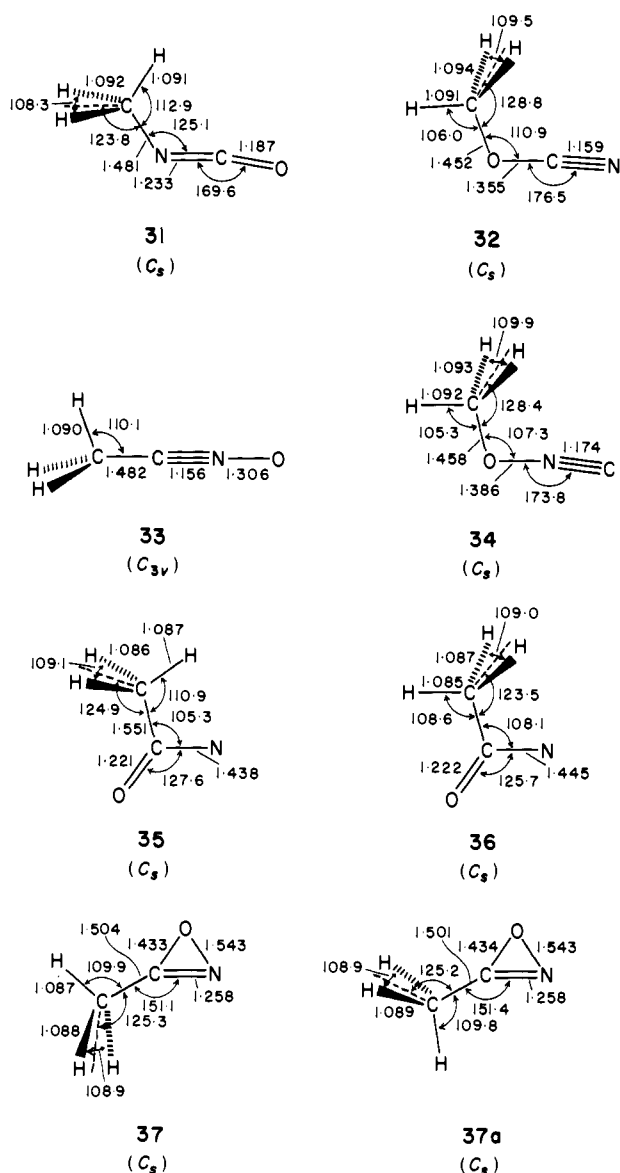


30a

(C_s → C_{2v}, 4-31G,
E = -192.76043)

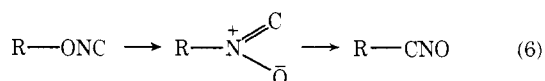
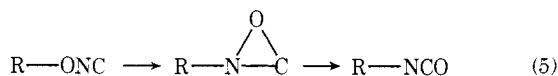
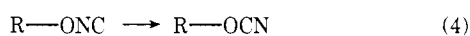
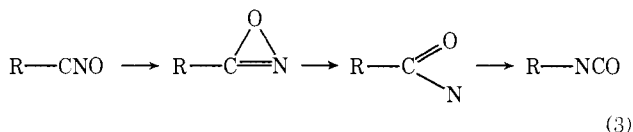
carried out. At the STO-3G level, the optimum structure is planar and trans bent (30). However, our better 4-31G calculations yield a structure (30a) with a linear heavy atom chain and overall C_{2v} symmetry.

R = CH₃. Theoretical calculations on acetonitrile oxide¹⁸ and acetylnitrene^{19,20} have been reported previously but without full geometry optimization. Our fully optimized structures for the methyl substituted isomers 31-37 do not differ greatly from those expected on the basis of fragment structures. Methyl isocyanate (31), methyl cyanate (32), and methyl fulminate (34) are all trans bent but to a lesser extent than in the parent compounds. The increase (10.5°) in the calculated CNC angle in methyl isocyanate (125.1°) over the value of the HNC angle in isocyanic acid (114.6°) is in reasonable agreement with the experimental difference (11.9°),^{21,22} although the individual angles are both underestimated at the STO-3G level of theory. The experimental angles are 140.0 and 128.1°, respectively. The increase in the N-O length of acetonitrile oxide (33) (1.306 Å) compared with formonitrile oxide (16) (1.294 Å) again agrees with results of microwave spectral studies²³⁻²⁵ for the two molecules. Both N-O lengths are substantially greater than the experimental values (1.219 and 1.199 Å, respectively), a shortcoming previously recognized^{2,26} for minimal basis set treatments of dative N-O bonds. The theoretical dipole moment of acetonitrile oxide (4.47 D) is considerably larger than in formonitrile oxide (3.62 D), again reproducing the experimental results^{23,27} (4.49



vs. 3.06 D). The conformation (**35**) of acetylnitrene with a methyl C-H eclipsing the C-N single bond is marginally favored over the one (**36**) in which the C-H eclipses C=O. In methyloxazirine the favored conformation (**37a**) has the expected arrangement of C-H eclipsing the C=N double bond. We may note at this point that, according to previous theoretical work, the ground state of acetylnitrene is a triplet.²⁰

The CH_3CNO isomers are of special interest as model compounds for higher alkylated RCNO isomers, many of which are known experimentally.^{28,29} We have therefore investigated the rearrangements 3-6 with $\text{R} = \text{CH}_3$, which had



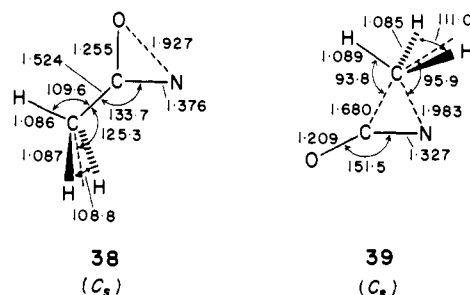
been studied previously² for the parent compounds ($\text{R} = \text{H}$). Pertinent data are shown in Table IV.

Table IV. Total Energies of Transition States and Intermediates

Structure	Type	Total energy, hartrees	
		STO-3G	4-31G
38	Transition state	-203.966 24	-206.328 09
39	Transition state	-203.972 02	-206.342 20
40	Intermediate ^a	-203.987 94	-206.257 37
41	Intermediate ^a	-203.976 27	-206.269 17
42	Transition state	-203.860 14	-206.233 18
62	Transition state	-239.238 96	-242.099 36
74	Transition state	-262.850 83	-266.064 34

^a Local C_{3v} symmetry assumed for OCH_3 and NCH_3 groups.

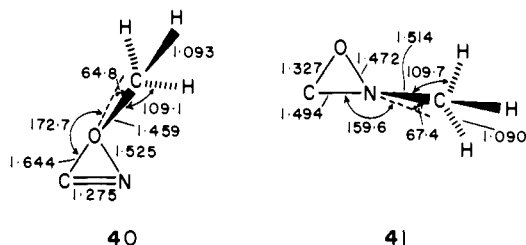
Transition state **38**, which links the methyloxazirine (**37**) and acetylnitrene (**35**) minima on the STO-3G potential energy surface, was obtained using the direct procedure⁵ for resolving transition states and found to lie 24 kcal mol⁻¹ above the cyclic isomer (**37**) (STO-3G). However, using the more reliable 4-31G basis set, **38** emerges 11 kcal mol⁻¹ below **37**,



i.e., the ring opening in methyloxazirine is predicted to occur without activation. Furthermore, the 4-31G calculations also suggest that the rearrangement of singlet acetylnitrene to methyl isocyanate via **39**, requires no activation (**39** being more stable than **35**). Thus, the rearrangement $\text{CH}_3\text{CNO} \rightarrow \text{CH}_3\text{NCO}$ is predicted to pass through structures which may be termed methyloxazirine and (singlet) acetylnitrene; however, these are *not* true intermediates and should not be observable compounds. Similar results have been obtained for the parent compounds.²

Neither methyloxazirine nor acetylnitrene has been characterized experimentally. However, our results do bear some relation to the extensive experimental material on apparent alkanoylnitrene reactions.²⁸ Pivaloylnitrene (**5**, $\text{R} = t\text{-Bu}$) has been examined in particular detail. Lwowski³⁰ has studied the photoinduced Curtius rearrangement of pivaloyl azide and found that the yield of *tert*-butyl isocyanate does not depend on the amount of typical "nitrene products" (*N*-alkylpivaloylamides, pivaloylamide) formed by reaction with hydrocarbon solvents. This implies that isocyanate formation and "nitrene product" formation are not competing processes. Lwowski's experiments can be interpreted in two different ways: (a) Singlet pivaloylnitrene is trapped by hydrocarbon solvents much faster than it rearranges to the isocyanate; the isocyanate precursor is possibly an excited acyl azide.³¹ (b) Singlet pivaloylnitrene rearranges much faster than it can be trapped by the solvent; the "nitrene product" precursor is possibly triplet pivaloylnitrene or an excited acyl azide. There seems to be general consent that (a) is correct, although conclusive proof has not yet been published. Insofar as our theoretical results for acetylnitrene are representative of other alkanoylnitrenes, they support interpretation (b).

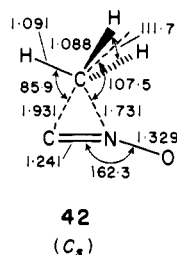
The rearrangement $\text{CH}_3\text{ONC} \rightarrow \text{CH}_3\text{OCN}$ (eq 4, $\text{R} = \text{CH}_3$) was studied in less detail. As a model for the transition state we use **40**, which is a true intermediate on the STO-3G potential surface, but probably not at the 4-31G level (cf. the discussion of the analogous rearrangement $\text{HONC} \rightarrow \text{HOCN}$ in ref 2). The activation energy estimated in this way is 43 kcal



mol^{-1} (4-31G), essentially the same as for $\text{R} = \text{H}$ (39 kcal mol^{-1}).

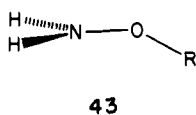
Similarly, our experience² with the parent compounds suggests that the intermediate **41** may be used to arrive at a lower limit for the activation energy of the $\text{CH}_3\text{ONC} \rightarrow \text{CH}_3\text{NCO}$ rearrangement (eq 5, $\text{R} = \text{CH}_3$). This estimate is 50 kcal mol^{-1} , compared with 51 kcal mol^{-1} for $\text{R} = \text{H}$.

Finally, the activation barrier for the process $\text{CH}_3\text{ONC} \rightarrow \text{CH}_3\text{CNO}$ (eq 6, $\text{R} = \text{CH}_3$; transition state **42**) is 66 kcal

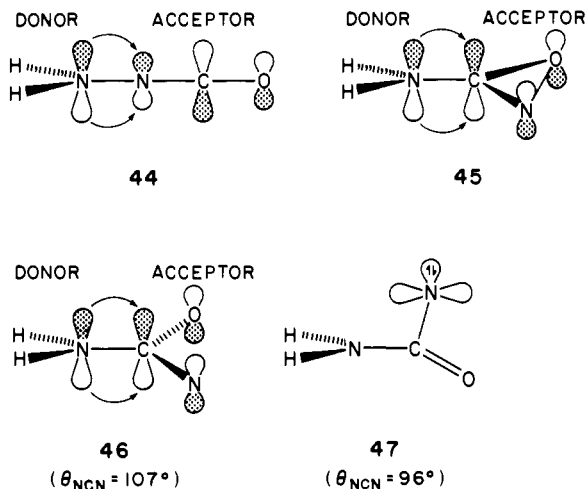


mol^{-1} , slightly less than the value calculated for $\text{R} = \text{H}$ (73 kcal mol^{-1}). We therefore conclude that methyl fulminate is reasonably stable toward intramolecular rearrangements and should be an observable compound, provided that complicating intermolecular reactions can be suppressed.

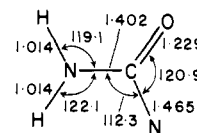
$\text{R} = \text{NH}_2$. The amino substituent was approximated by a planar model geometry, and two conformations (planar and perpendicular) were investigated in each case. H_2NOCN and H_2NONC can be viewed as substituted hydroxylamines **43** ($\text{R} = \text{CN}$ or NC) and adopt perpendicular conformations corresponding to the optimum theoretical structure of the parent compound (**43**, $\text{R} = \text{H}$).³² The remaining isomers prefer con-



formations which allow bonding interaction between the substituent lone pair and the lowest unoccupied orbital of the CNO fragments. We note that the energy difference between planar and perpendicular conformations of **44** and **45** parallels the LUMO amplitude at the key atom of the acceptor fragments. However, the planar conformation (**46**) of aminocar-



bonylnitrene is only 4 kcal mol^{-1} more stable than the perpendicular structure **47**. In this case the large difference in NCN bond angles suggests some N-N bonding in **47**. Since such bonding would also stabilize the transition state for the rearrangement of perpendicular aminocarbonylnitrene to aminyl isocyanate (NH_2NCO), we checked whether the aminocarbonylnitrene structures correspond to true minima on the potential energy surface. Upon full optimization at the STO-3G level **47** collapsed without activation to aminyl isocyanate, whereas planar aminocarbonylnitrene turns out to be a stable structure (**46a**). The energy difference between **46**

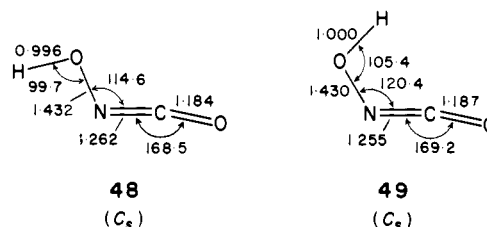


46a
(C_s , STO-3G, $E = -219.71818$)

and **47** can then be taken as an upper limit for the theoretical (STO-3G) barrier for the aminocarbonylnitrene-aminyl isocyanate rearrangement. This estimate is low, 4 kcal mol^{-1} , and suggests that singlet aminocarbonylnitrene rearranges faster than it can be trapped by intermolecular reactions. Experimental results concerning this point are scarce. The thermal and photochemical Curtius rearrangement of carbamoyl azides is believed not to involve a nitrene intermediate.³³ Several reactions are known which yield products suggestive of an aminocarbonylnitrene intermediate, but their mechanisms have not been investigated in detail.³⁴

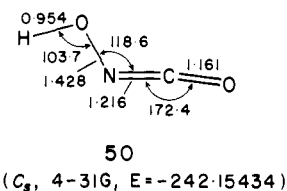
$\text{R} = \text{OH}$. The hydroxy-substituted HCNO isomers were investigated in greater detail because of their close relation to species potentially involved in the chemistry of alkoxy carbonylnitrenes. We find that the effect of an OH substituent is generally similar to, but more pronounced than, the effect of an amino group.

The most stable HO(CNO) isomer is hydroxyl isocyanate **50**. It adopts a W-shaped, planar configuration. The NCO



48
(C_s)

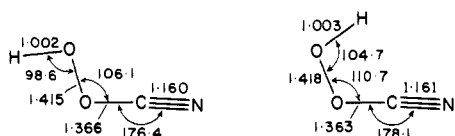
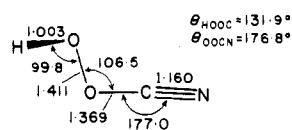
49
(C_s)



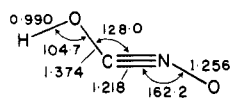
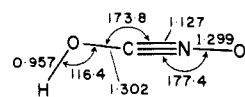
50
(C_s , 4-31G, $E = -242.15434$)

chain is slightly nonlinear as in isocyanic acid. The hydroxyl cyanate molecule (**51-53**) may alternatively be viewed as a cyano-substituted hydrogen peroxide. Internal rotation about the O-O bond leads to potential minima for trans (**51**) and skew (**53**) structures. Calculations on intermediate structures show that the potential function is virtually completely flat in the interval between **51** and **53**.

Our best calculations suggest that HOCNO (**55**) is less stable than the tautomeric hydroxyl isocyanate (**50**) by 40 kcal mol^{-1} . As expected for an *N*-oxide of cyanic acid, **55** has a slightly nonlinear heavy atom chain. At the STO-3G level (**54**) the distortion from linearity in the OCN angle is very large. Further calculations would be desirable to establish whether or not this is simply an artifact of the small basis set.

51
(C_s)52
(C_s)

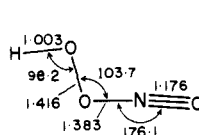
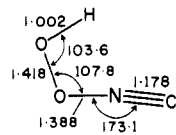
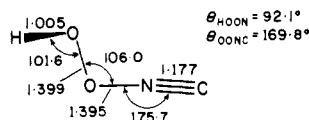
53

54
(C_s)

55

(C_s, 4-31G, E = -242.09061)

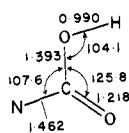
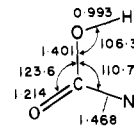
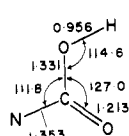
For hydroxyl fulminate, the favored structure is skew (58). We may note that the π -acceptor properties of the CN and NC groups in 53 and 58 lead to a reduction of the repulsion between

56
(C_s)57
(C_s)

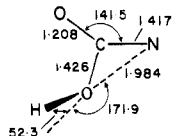
58

lone pairs on adjacent oxygen atoms and hence to a significant shortening of the O-O bond length (in H₂O₂: 1.468 Å, STO-3G³²).

Owing to the very weak O-O single bond, the peroxides 53 and 58 are less stable than hydroxycarbonylnitrene (59). Our best calculations (4-31G optimized geometries) indicate that hydroxycarbonylnitrene (61) lies just 20 kcal mol⁻¹ above

59
(C_s)60
(C_s)

61

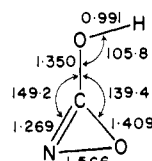
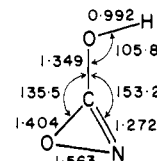
(C_s, 4-31G,
E = -242.12170)

62

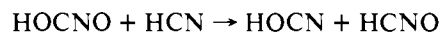
hydroxyl isocyanate (50). The corresponding value² for the parent compounds is 88 kcal mol⁻¹. Unlike formylnitrene and acetylnitrene, singlet hydroxycarbonylnitrene (61) is found to be a true minimum on the 4-31G potential energy surface. The theoretical barrier for the rearrangement hydroxycarbonylnitrene \rightarrow hydroxyl isocyanate (transition state 62) is 5.8

kcal mol⁻¹ (4-31G/STO-3G). The apparent inability of singlet alkoxy carbonylnitrenes to arrange to alkoxy isocyanates²⁸ can perhaps be ascribed to the weakness of the developing N-O single bond, coupled with facile intersystem crossing to a triplet ground state and subsequent dissociation. Theoretical work suggests that methoxycarbonylnitrene has a triplet ground state.²⁰ The ground state of ethoxycarbonylnitrene is a triplet.³⁵

Since the hydroxy substituent stabilizes the carbonylnitrene structure more than oxazirine, and since it is not directly involved in the oxazirine \rightarrow carbonylnitrene rearrangement, there is no reason to expect hydroxyoxazirine to be kinetically more stable than methyloxazirine or the parent oxazirine. Optimization studies at the 4-31G level do in fact suggest that hydroxyoxazirine rearranges without activation to hydroxycarbonylnitrene and should therefore not be an observable compound. We have no doubt that calculations on alkoxyoxazirines will produce the same result.³⁶

63
(C_s)64
(C_s)

We have already commented on the destabilization of the nitrile oxide fragment by the σ acceptor OH (cf. the negative stabilization energy in Table III). Cyanic acid shows a similar effect¹⁵ which is smaller, however, because the N-oxygen is a σ acceptor and π donor and thus weakens the π -acceptor properties of the cyano group while increasing its σ -acceptor strength. As a result, the oxygen transfer reaction

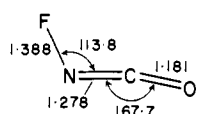


$$\Delta E(4-31G) = -19 \text{ kcal mol}^{-1}$$

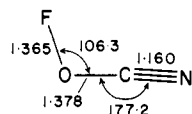
is exothermic, and we predict compounds ROCNO to be stronger oxidizing agents than the corresponding nitrile oxides RCNO. Furthermore, since the transition state for the nitrile oxide \rightarrow isocyanate rearrangement resembles oxazirine,² and since the hydroxy substituent stabilizes the oxazirine structure but destabilizes the nitrile oxide, we expect alkoxy-substituted nitrile oxides to rearrange more easily to the isocyanates than alkylated nitrile oxides.

R = F. The order of stabilities of the fluorine substituted isomers, and in particular the low energy of fluorocarbonylnitrene, has been discussed above. Fluorine isocyanate (65), fluorine cyanate (66), and fluorine fulminate (70) have the expected trans bent structures. The minimal STO-3G basis set predicts a very flat bending potential for FCNO with a shallow (2.5 kcal mol⁻¹) dip at a trans bent geometry 67. This is possibly an artifact of the minimal basis set and caused by too high a ratio between the number of electrons and the number of basis functions. The extended 4-31G basis set predicts a linear equilibrium structure 68 for FCNO and we regard this result as more reliable. We may also note that our calculations predict a triplet ground state for FCNO (49 kcal mol⁻¹ below the singlet), which may be represented as 73. However, in view of our use of rather small basis sets and the single determinant approach, refined calculations on FCNO are required before firm conclusions can be drawn.

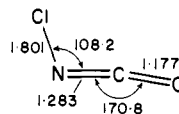
Previous ab initio work²⁰ had suggested a triplet ground state for fluorocarbonylnitrene. Our calculations predict that, in its lowest single state, fluorocarbonylnitrene corresponds to a true minimum (71a) in the potential energy surface. However, the transition state 74 for the rearrangement to fluorine isocyanate is only slightly above the nitrene (4-31G: 7.6 kcal mol⁻¹).



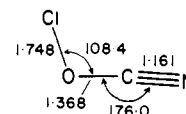
65
(C_s)



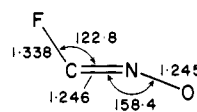
66
(C_s)



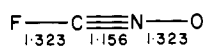
75
(C_s)



76
(C_s)



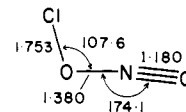
67
(C_s)



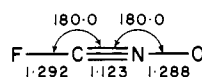
67a
($C_{\infty v}$)



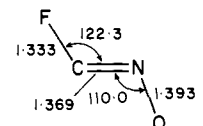
77
($C_s \rightarrow C_{\infty v}$)



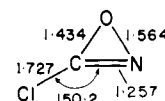
78
(C_s)



68
($C_s \rightarrow C_{\infty v}$, 4-31G,
 $E = -266.04324$)

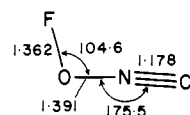


69
(C_s)

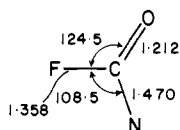


79
(C_s)

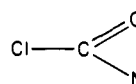
CIONC (78). However, presumably because of the relatively low electronegativity of chlorine, intermediate structures like **80a** are also quite stable and chlorocarbonylnitrene (**79**) is



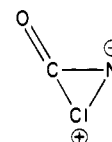
70
(C_s)



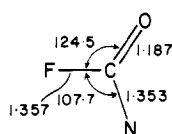
71
(C_s)



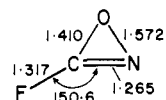
80



80a



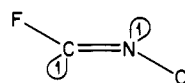
71a
(C_s , 4-31G,
 $E = -266.08588$)



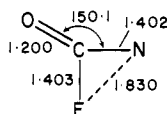
72
(C_s)

found to rearrange without activation, even at the STO-3G level, to the isocyanate **75**. There appears to be no experimental information on the possible existence of chlorocarbonylnitrene. Attempts to prepare chloroformonitrile oxide have resulted in the formation of the dimer, dichlorofuroxane.³⁹

$R = CN$. With the exception of cyanoformonitrile oxide (**83**), which has been trapped by 1,3-dipolar reactions,⁴¹ and cyanogen isocyanate (**81**),⁴¹ none of the cyano-substituted



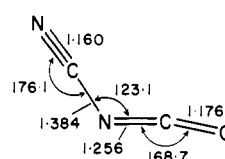
73



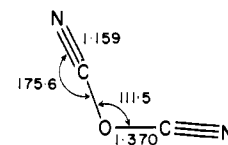
74
(C_s)

$R = Cl$. Our optimum structure for chlorine isocyanate (**74**) is in moderate agreement with the experimental structure derived from microwave data.³⁷ Of particular importance is the NCO angle, which is almost exactly reproduced (170.8° vs. 171.4°), and this lends some credence to our finding that isocyanates are generally (a notable exception being lithium isocyanate) trans bent. Previous CNDO/2 calculations^{16,38} on CINCNO have also produced a trans bent equilibrium structure.

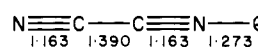
The chlorine substituent is, in its effect on the relative energy of RCNO isomers, intermediate between the hydroxy and amino groups. Calculated at a model geometry, chlorocarbonylnitrene (**80**) is slightly more stable than chloroformonitrile oxide (**77**), and chlorooxazirine **79** is more stable than



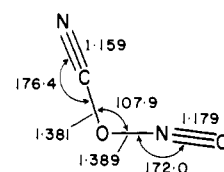
81
(C_s)



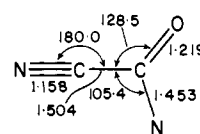
82
($C_s \rightarrow C_{2v}$)



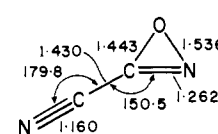
83
($C_{\infty v}$)



84
(C_s)



85
(C_s)



86
(C_s)

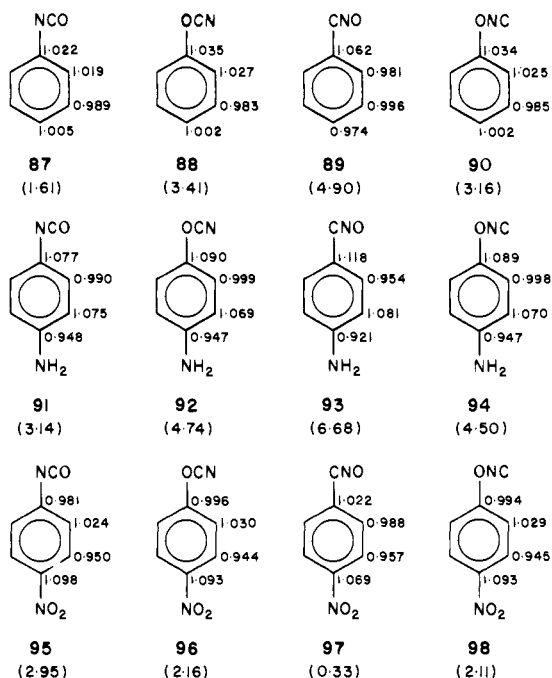


Figure 2. π -Electron populations and dipole moments (D, following structure number).

RCNO isomers have been observed experimentally. The microwave spectrum of **81** has been measured and indicates a bent structure,⁴² in disagreement with earlier IR measurements⁴³ which had suggested that NCNCO is linear in the gas phase. Our fully optimized structure for cyanogen isocyanate is strongly bent at the central nitrogen atom and thus supports the preliminary interpretation of the microwave spectrum.⁴²

The order of stabilities of RCNO isomers is the same for R = CN and for R = CH₃. Presumably because of its σ -acceptor properties, the cyano group does not, as could have been assumed, stabilize the "antiaromatic" oxazirine relative to the carbonylnitrene. We also note that the cyano group stabilizes the isocyanate structure more than the cyanate and carboxime isomers, apparently because a nitrogen lone pair is a better π donor than an oxygen lone pair.

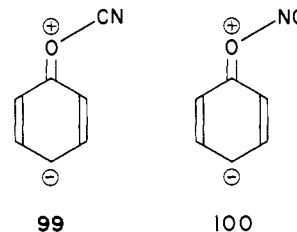
R = C₆H₅, *p*-NH₂C₆H₄, *p*-NO₂C₆H₄. The phenyl, *p*-aminophenyl, and *p*-nitrophenyl substituents were examined as prototypes for general aromatic derivatives of isocyanates, cyanates, nitrile oxides, and fulminates. In analyzing our results, it is useful to consider, in addition to the structural and energetic data of Table I, π -electron distributions calculated using the Mulliken approach.⁴⁴ These are shown together with directly evaluated dipole moments in Figure 2.

There has been some disagreement in the literature as to the equilibrium structure of phenyl isocyanate. Dipole moment^{45,46} and infrared and Raman spectral⁴⁷ studies suggested a structure with a linear Ph-N-C-O group and C_{2v} symmetry. However, more recent microwave investigations^{48,49} and INDO molecular orbital calculations⁴⁹ have favored a planar C_s structure with a Ph-N-C angle of about 140°. If the values of the other geometric parameters are assigned values on the basis of data for related molecules, the microwave rotational constants lead⁴⁸ to C(phenyl)-N = 1.37 Å and Ph-N-C = 140.6°. Our calculations also indicate (Table I) a C_s rather than C_{2v} structure for phenyl isocyanate, although, as for methyl isocyanate, the C-N bond length is overestimated and the Ph-N-C angle underestimated.

An x-ray crystal structure has been determined for 4-methoxy-2,6-dimethylbenzotrile oxide.⁵⁰ The C(aryl)-C(nitrile oxide) bond length is 1.435 Å compared with our value of 1.454 Å. The experimental N-O length in this molecule (1.249 Å)

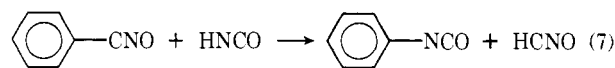
is somewhat longer than the experimental N-O length (1.199 Å) in formonitrile oxide itself.²³ Because of the lower symmetry due to the substituents in 4-methoxy-2,6-dimethylbenzotrile oxide, the slight deviations from linearity found for the Ar-C-N (173.8°) and C-N-O (178.3°) bonds are not considered significant in the context of the structure of benzotrile oxide itself.

Experimental structures are not available for either phenyl cyanate or phenyl fulminate. Our calculations indicate that phenyl substitution leads to an opening of the bond angle at O in each case, a result which can be easily rationalized in terms of contributions from valence structures of the type **99** and **100**.



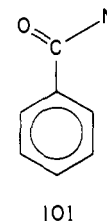
Indeed, the calculated π -electron distributions (Figure 2) with negative charges at the ortho and para positions support such contributions. The C(phenyl)-O bond lengths are accordingly shorter than the C(methyl)-O lengths in the corresponding methyl derivatives.

The phenyl and substituted phenyl substituents do not have a marked effect on the relative stabilities of the R(CNO) isomers. In the case of the phenyl substituent, the only significant effect is the relative stabilization of the nitrile oxide relative to the other isomers. Thus, for example, the calculated energy change in reaction 7 is 8.0 kcal mol⁻¹.



Relative to the other three isomers, benzotrile oxide is stabilized by a *p*-amino substituent and destabilized by *p*-nitro substitution. This result is consistent with the π -electron-accepting nature of the CNO group as opposed to the π -electron donor properties of NCO, OCN, and ONC groups.

Benzoylnitrene (**101**) is predicted to lie 85 kcal mol⁻¹ above



phenyl isocyanate, almost identical with the 86 kcal mol⁻¹ energy difference in the parent molecules. We have not examined explicitly whether or not benzoylnitrene will be stable with respect to collapse to phenyl isocyanate. Experimental work⁵¹ on the photolysis of benzoyl azide in cyclohexane may be interpreted in terms of initial formation of benzoylnitrene as a singlet with low-energy pathways to the triplet and to phenyl isocyanate. In an efficient singlet trap, a major product is the CH insertion product. In a less effective singlet trap (e.g., cyclohexane), the singlet is able to either rearrange to the isocyanate or to undergo intersystem crossing to the triplet. These two processes appear to be competing.⁵² An alternative interpretation⁵¹ of the experimental results maintains that the nitrene is not the isocyanate precursor. More direct evidence on this point is clearly desirable.

The calculated dipole moments of the nitrile oxides are of interest. The moment for benzotrile oxide is 4.90 D, which is significantly greater than the STO-3G value⁵³ (3.65 D) for benzotrile itself. In a similar manner, the STO-3G calculated

moments for acetonitrile oxide (4.47 D) and formonitrile oxide (3.62 D) are appreciably larger than corresponding values for acetonitrile (3.06 D) and hydrogen cyanide (2.45 D). These results, however, are in conflict with experimental determinations which show that dipole moments of nitrile oxides and corresponding nitriles are generally quite similar.⁵⁴ The discrepancy may be associated with the overestimation (by STO-3G) of the N–O length in formonitrile oxide² and other N-oxides.²⁶ The use of a shorter N–O bond would be likely to result in decreased calculated moments. The large increase in dipole moment in benzonitrile oxide on *p*-amino substitution and large decrease on *p*-nitro substitution correspond respectively to reinforcing and opposing π -electron effects.

Summary and Conclusions

We have used ab initio molecular orbital theory to examine substituted isocyanates, cyanates, nitrile oxides, fulminates, carbonylnitrenes, and oxazirines in their lowest singlet states. Substituents considered include Li, BH₂, CH₃, NH₂, OH, F, Cl, CN, C₆H₅, *p*-NH₂C₆H₄, and *p*-NO₂C₆H₄. Our main results follow.

(a) The Li-substituted systems, LiNCO, LiOCN, and LiONC, are each predicted to be linear molecules. The other isocyanates (RNCO), cyanates (ROCN), and fulminates (RONC) are all predicted to have trans or skew bent structures. The theoretical data are in line with experimental evidence that C₆H₅NCO and NCNCO have C_s structures, and are in essential agreement with microwave data for CINCO. The CNO fragment in HOCNO is found to be slightly nonlinear.

(b) No substituent was found which would stabilize the fulminate (RONC) structure significantly. However, methyl fulminate (CH₃ONC) is predicted to be about as stable as acetonitrile oxide (CH₃CNO) and should be observable under suitable conditions.

(c) The acetonitrile oxide \rightarrow methyl isocyanate rearrangement is found to involve no metastable intermediates.

(d) Singlet acetylnitrone and chlorocarbonylnitrone are predicted to collapse without activation to the isocyanates. On the other hand, hydroxycarbonylnitrone, the parent compound of carbalkoxy nitrenes, and fluorocarbonylnitrone are found to be low-energy stable isomers, although they lie in relatively shallow potential wells.

(e) There is no theoretical evidence for a substituted oxazirine which would be stable enough to be observable.

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- (11) 4-31G energies for structures fully (when available) or partially (otherwise) optimized at the STO-3G level. UHF/4-31G energies for R + C + O + N (all fragments in their ground states) are -167.169 60 (H), -174.098 69 (Li, 5-21g), -192.374 11 (BH₂), -206.174 74 (CH₃), -222.144 06 (NH₂), -241.955 71 (OH), -265.935 80 (F).
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