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STRUCTURE AND REACTIONS OF N,N'-BIS(2-ISOCYANATO-2-PROPYL) DIAZENE (1)*

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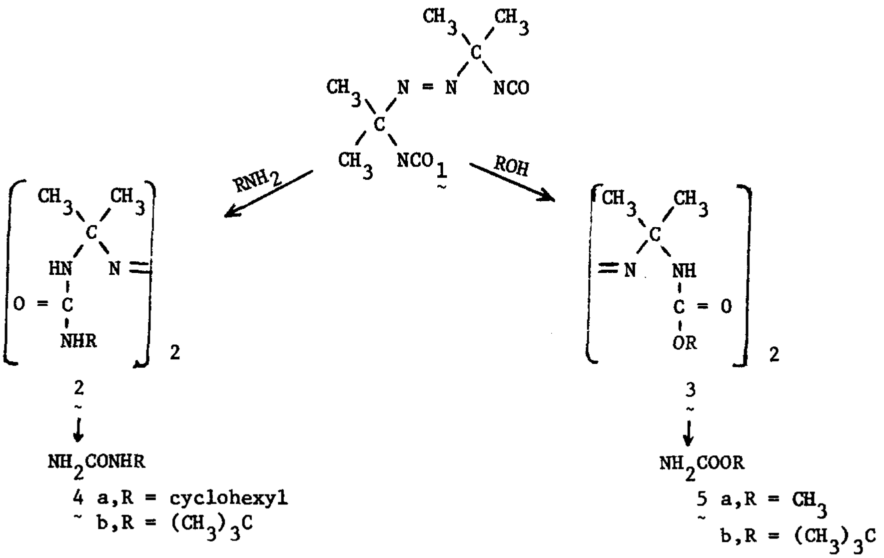
The ability to crosslink polymers is of considerable industrial interest.[1] To this end we have investigated the structure, chemical reactions and thermal stability of 2,2'-diisocyanato-2,2'-azopropane (1) which is a potential free radical source and has a reactive functional group built into the initiator. As such, a monomer unit could be attached to the initiator or the initiator could itself be incorporated into the polymer.

Both this compound (1) and its thiocyanate analog have been reported in the patent literature.[2] However, because of the unusual chemical reactivity (reported herein) and the paucity of structural evidence it was deemed necessary to establish whether the correct structure was that of the cyanate (-O-C≡N) or isocyanate (-N=C=O) linkage. This compound was prepared in 12% yield according to the literature[2]: mp 59-60°C; NMR δ 1.58 ppm (s); IR 2232 cm^{-1}; UV λ_{max} 337 nm, ε=10.

Two characteristic reactions were considered useful in the structure elucidation of 1 and in linking the initiator to the polymer backbone; the reaction with amines to form bis-azo-ureas (2) and the reaction with alcohols to form bis-azo-urethanes (3). While we have obtained spectroscopic evidence for the formation of several of these intermediate adducts (2b and 3a), normal workup procedures led only to the isolation of ureas (4) and carbamates (5). We have made little attempt to determine the mechanism of fragmentation. However, no acetone azine or azoisopropane could be detected under optimized gas chromatographic conditions that would have observed less than 2%. This would seem to rule out the concerted breakage of both C-NHCONHR bonds.

By contrast the diisocyanate (1) was a remarkably stable compound which showed no appreciable decomposition at temperatures below 100°C. It decomposed with quantitative evolution



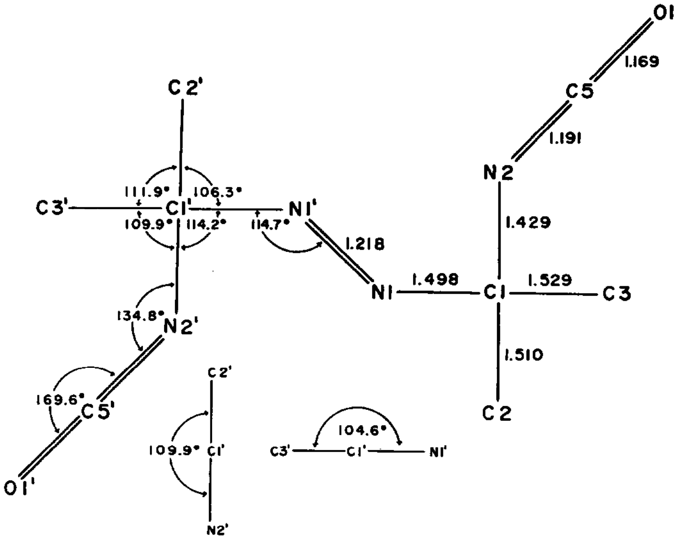
of nitrogen and showed good first order kinetics between 130° and 160°C (diphenyl ether $\Delta H^{\ddagger} = 36.5$ kcal/mol, $\Delta S^{\ddagger} = 12.4$ eu). The $t_{1/2\ 140^{\circ}} = 50$ min while that of AIBN $\simeq$ 8 sec.[3]

Because no stable functionalized derivatives of 1 could be prepared to satisfactorily establish the structure of the isocyanate we undertook a x-ray study[4] of a single crystal grown from chloroform.

Figure 1, a stick drawing of the molecule, shows all of the distances and angles for the non-hydrogen atoms. Estimated standard deviations (esd) are 0.006-.007 A° for bond distances not involving hydrogen and 0.4-0.6° for CCH angles; and 0.8-1.4° for HCH angles.

The molecular parameters obtained in this study are internally consistent with analogous parameters found in structural studies on azobisisobutyronitrile (AIBN-two crystalline modifications),[5] azobis-3-cyano-3-pentane (ACP),[5] and 1,1'-dichloro-1,1'-diphenyl-1,1'-azopropane.[6] To our knowledge this is the first x-ray crystal structure reported for an isocyanate derivative. In view of the known linearity of allenic systems and earlier reports for HNCO,[7] CH_3NCO[8] and NCNCO[9] linearity might have been expected here.
Clearly this is not the case and our results of a transoid structure for 1 with a C-N=C angle of 134.8° and a N=C=O angle of 169.6° are in keeping with more recent microwave, electron diffraction and theoretical studies on HNCO,[10] ClNCO,[11] CH_3NCO[12] and NCNCO.[13] The value of 169.6° agrees nicely with all determinations and the 134.8° angle falls between the values of 128° for HNCO and 140° for CH_3NCO.

The fact that no close-contacts ($\leq$3.50 A°) between molecules are observed and the consistency between our crystal study and those done in the gas phase rules out any distortions due to crystal packing.


O1
1.169
C5
1.191
N2
C2'
111.9°
106.3°
C3'
C1'
N1'
109.9°
114.2°
114.7°
1.218
1.429
N1
1.498
C1
1.529
C3
134.8°
N2'
1.510
169.6°
C5'
C2
O1'
C2'
104.6°
109.9°
C1'
C3'
C1'
N1'
N2'

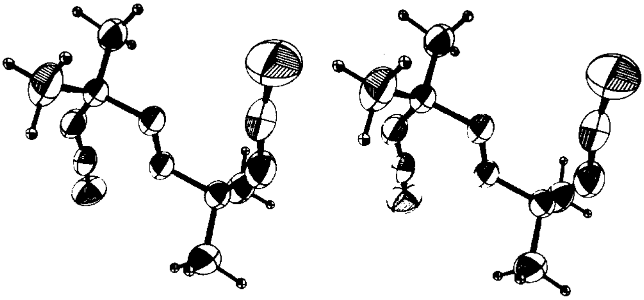


Table 1

Space-Group Bond Lengths Å	This study	AIBN[5]		ACP[5]	CPAP[6]	HNCO[7]	CH_3NCO[8]
	$P\bar{1}$	$P\bar{1}$	$P2_{1/c}$	C_{mca}	$P\bar{1}$	——	——
N=N	1.218(6)	1.223(4)	1.217(3)	1.218(4)	1.24	——	——
=N-C	1.498(5)	1.501(3)	1.492(3)	1.496(4)	1.47	——	——
C-C	1.510(5)	1.513(4)	1.522(3)	1.538(5)	1.56		
	1.529(6)	1.518(4)	1.524(3)	1.481(8)	1.57		
N=C	1.191(5)	——	——	——	——	1.209	1.225
C=O	1.169(5)	——	——	——	——	1.166	1.162
Bond Angles (Deg.)							
N=N-C	114.7	114.2	114.8	115.2	116	——	——
=N-C-C	106.3	106.6(2)	106.9(2)	107.2(3)	107	——	——
	111.9	——	——	——	——		
	104.6	106.6(2)	106.9(2)	107.2(2)	108		
C-N=C	134.8	——	——	——	——	128°	140°
N=C=O	169.6	——	——	——	——	180*	180*

*assumed

References and Notes

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