Azidocarbonyl-substituted Cubanoureas

Richard Gilardi*, Clifford George and Jerome Karle

Laboratory for the Structure of Matter, Naval Research Laboratory,
Washington, D. C. 20375-5341, USA

Philip E. Eaton and Munagala Rao

Department of Chemistry, The University of Chicago,
5735 S. Ellis Ave., Chicago, Illinois 60637

Received May 14, 1993

Dedicated to the memory of Dr. Roland K. Robins

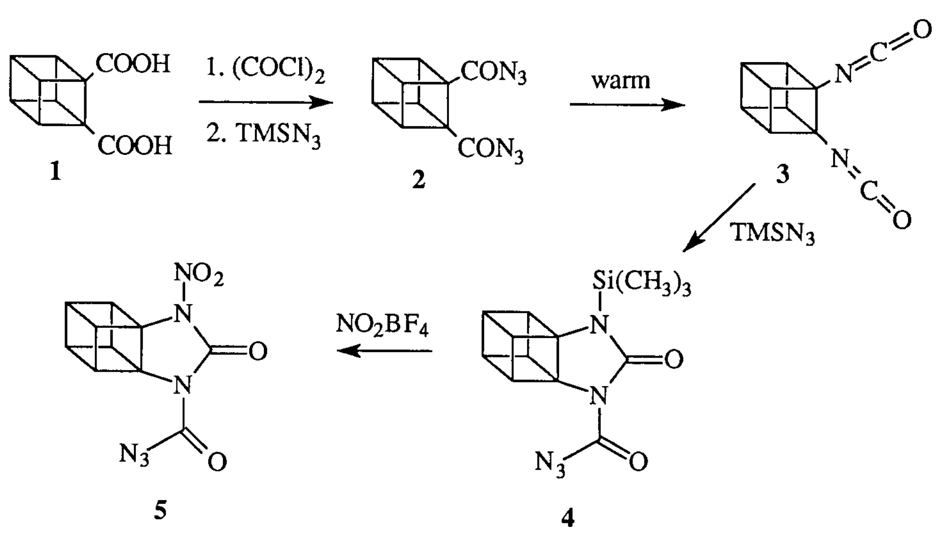
Despite the angular strain associated with the assembly of small rings, 1,2-diisocyanatocubane reacts with trimethylsilyl azide under mild conditions to form a hexacyclic ring assembly that contains an imidazolidone ring fused to one edge of cubane. This compound was identified as an azidocarbonyl-substituted cubanourea by means of X-ray crystal structure analysis of the nitro-derivative, the energetic compound *N*-azidocarbonyl-*N'*-nitrocubanourea.

J. Heterocyclic Chem., **30**, 1389 (1993).

There is substantial interest in the preparation of nitrated cubanes for it is expected that these materials will prove to be shock-insensitive, high-density explosives of great power [1]. Excellent methodology has been developed for the preparation of carboxylated cubanes [2] and for their conversion into nitrocubanes [3]. As detailed elsewhere [3], a Curtius-type rearrangement of acyl azides (*e.g.*, **2**) is used to get nitrogen attached directly to the cubane nucleus (see Scheme 1). When there are adjacent carboxyl groups on the nucleus, as in **1**, the conversion to the desired isocyanate can be much less high-yielding than with other carboxycubanes, even those containing three or four non-adjacent carboxyl groups [4]. The interfering side-reaction is now understood to arise from the attack of excess trimethylsilyl azide on the intermediate 1,2-diisocyanate **3** with closure to the azidocarbonyl urea **4**, a derivative of cubanourea [5]. Nitrolysis of **4** with nitronium tetrafluoroborate gives the interesting high-nitrogen compound **5** in excellent yield. This was characterized by X-ray crystallography.

The X-ray determination proceeded with no assumptions as to the nature of **5**, although an approximate empirical formula was used, and a di-substituted cubane was considered to be highly likely. Analysis of the diffraction data by direct methods yielded a preliminary result containing the 'atomic topology' of **5**, identical to that shown in Figure 1. Since both isocyanato and azido groupings were reported to be in the starting mixture, each was considered as a possibility for the assignment of the identity of the linear terminal group. The two groups are isoelectronic and could appear very similar in electron density maps. The Cambridge Structural Database [CSD, 6] contains seven well-determined (agreement factor, R, <0.08) molecules containing an azido group connected to a tri-

Scheme 1



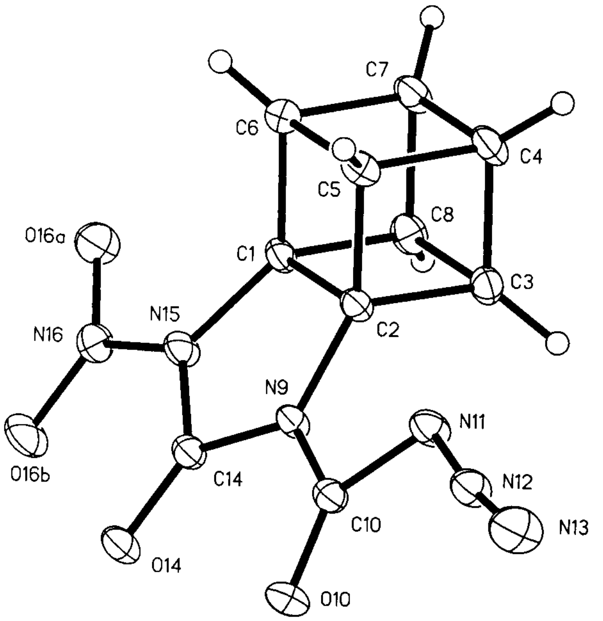


Figure 1. A thermal ellipsoid plot of *N*-Azidocarbonyl-*N'*-nitrocubanourea with ellipsoids drawn at the 20% probability level.

gonal carbon atom and only three with isocyanato groups. The average structures of these groups differ primarily in the value of the bond angle at the innermost atom, the one bonded to the backbone (N11 in **5**, see Figure 1); the average azido C-N-N angle for the CSD structures is 115° (range: 112 to 121°), and the corresponding average isocyanato C-N-C angle is 142° (range: 135 to 154°). For comparison, the observed C10-N11-N12 angle in **5** is 112.4(2)°, thus falling in the azido range. Chemical mechanistic reasoning and comparisons of other structural parameters also point to the same assignment of atoms.

Table 1. Bond lengths (Å) and angles (°) for molecule 5

C(1)-C(2)	1.522 (3)	C(1)-C(6)	1.546 (3)
C(1)-C(8)	1.556 (4)	C(1)-N(15)	1.429 (3)
C(2)-C(3)	1.548 (3)	C(2)-C(5)	1.543 (3)
C(2)-N(9)	1.443 (3)	C(3)-C(4)	1.557 (3)
C(3)-C(8)	1.578 (3)	C(4)-C(5)	1.560 (4)
C(4)-C(7)	1.551 (3)	C(5)-C(6)	1.573 (4)
C(6)-C(7)	1.559 (4)	C(7)-C(8)	1.563 (3)
N(9)-C(10)	1.377 (3)	N(9)-C(14)	1.407 (3)
C(10)-O(10)	1.202 (3)	C(10)-N(11)	1.415 (3)
N(11)-N(12)	1.254 (3)	N(12)-N(13)	1.120 (3)
C(14)-O(14)	1.196 (3)	C(14)-N(15)	1.414 (3)
N(15)-N(16)	1.387 (3)	N(16)-O(16A)	1.216 (3)
N(16)-O(16B)	1.217 (3)		

C(2)-C(1)-C(6)	90.8(2)	C(2)-C(1)-C(8)	90.8(2)
C(6)-C(1)-C(8)	92.5(2)	C(2)-C(1)-N(15)	103.0(2)
C(6)-C(1)-N(15)	133.1(2)	C(8)-C(1)-N(15)	131.2(2)
C(1)-C(2)-C(3)	91.3(2)	C(1)-C(2)-C(5)	91.1(2)
C(3)-C(2)-C(5)	92.6(2)	C(1)-C(2)-N(9)	106.2(2)
C(3)-C(2)-N(9)	130.2(2)	C(5)-C(2)-N(9)	132.1(2)
C(2)-C(3)-C(4)	87.9(2)	C(2)-C(3)-C(8)	89.0(2)
C(4)-C(3)-C(8)	89.6(2)	C(3)-C(4)-C(5)	91.6(2)
C(3)-C(4)-C(7)	90.6(2)	C(5)-C(4)-C(7)	90.3(2)
C(2)-C(5)-C(4)	88.0(2)	C(2)-C(5)-C(6)	89.1(2)
C(4)-C(5)-C(6)	89.6(2)	C(1)-C(6)-C(5)	89.1(2)
C(1)-C(6)-C(7)	88.1(2)	C(5)-C(6)-C(7)	89.6(2)
C(4)-C(7)-C(6)	90.4(2)	C(4)-C(7)-C(8)	90.4(2)
C(6)-C(7)-C(8)	91.8(2)	C(1)-C(8)-C(3)	88.9(2)
C(1)-C(8)-C(7)	87.6(2)	C(3)-C(8)-C(7)	89.4(2)
C(2)-N(9)-C(10)	124.5(2)	C(2)-N(9)-C(14)	111.4(2)
C(10)-N(9)-C(14)	124.2(2)	N(9)-C(10)-O(10)	126.5(2)
N(9)-C(10)-N(11)	107.4(2)	O(10)-C(10)-N(11)	126.0(2)
C(10)-N(11)-N(12)	112.4(2)	N(11)-N(12)-N(13)	172.3(2)
N(9)-C(14)-O(14)	127.0(2)	N(9)-C(14)-N(15)	105.4(2)
O(14)-C(14)-N(15)	127.6(2)	C(1)-N(15)-C(14)	114.0(2)
C(1)-N(15)-N(16)	121.0(2)	C(14)-N(15)-N(16)	124.6(2)
N(15)-N(16)-O(16A)	115.3(2)	N(15)-N(16)-O(16B)	118.2(2)
O(16A)-N(16)-O(16B)	126.5(2)		

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 5

	x	y	z	U(eq)
C(1)	2279(4)	2964(2)	2043(2)	31(1)
C(2)	2287(4)	2436(2)	3494(2)	30(1)
C(3)	238(4)	1447(3)	3449(2)	36(1)
C(4)	1932(5)	128(3)	2929(2)	40(1)
C(5)	3982(5)	1124(3)	3020(2)	36(1)
C(6)	3973(5)	1664(3)	1520(3)	37(1)
C(7)	1925(5)	662(3)	1449(2)	40(1)
C(8)	217(4)	1990(3)	1944(2)	38(1)
N(9)	2474(3)	3780(2)	4258(2)	31(1)
C(10)	2575(4)	3787(3)	5619(2)	32(1)
O(10)	2532(3)	4884(2)	6315(2)	42(1)
N(11)	2707(3)	2261(2)	6058(2)	39(1)
N(12)	2812(4)	2145(2)	7294(2)	42(1)
N(13)	2932(5)	1874(3)	8375(3)	63(1)
C(14)	2509(4)	5089(3)	3438(2)	32(1)
O(14)	2571(3)	6371(2)	3789(2)	42(1)
N(15)	2468(3)	4564(2)	2120(2)	35(1)
N(16)	2367(3)	5493(2)	1002(2)	39(1)
O(16A)	2490(3)	4841(2)	-66(2)	48(1)
O(16B)	2180(3)	6856(2)	1170(2)	56(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Compound **5** contains the fused heterocycle/cubane assembly, cubanourea, whose structure was reported by Eaton *et al* [5] in its unsubstituted and *N,N'*-dinitro-substituted forms. All three compounds exhibit an unusual feature at the fusion site: the cube-edge shared with the heterocycle is significantly shorter than other edges of the cube. The length of the shared edge was reported to be 1.526(3)Å in cubanourea and 1.534(3)Å in *N,N'*-dinitrocubanourea. In **5**, the length of this bond [C(1)-C(2)] is only 1.522(3)Å, while the average of the other eleven cube-edge bonds in **5** is 1.558Å. The latter value is within the range reported in prior cubane structure determinations [7]. Thus this cubanourea contraction, while still unexplained, is consistent, and illustrates again that the cubane system is 'soft' in the sense that it is capable of substantial distortion without becoming unstable. We believe this determination (C1-C2 in **5**) is the shortest reported distance for a cubane edge bond. The longest reported distance for a cubane edge bond is 1.607Å [8], in a bulkily substituted phenylcubane.

Knowledge of the structures of **4** and **5**, and reasonable speculation as to their origin, has led to an improvement in methodology for the production of cubane isocyanates and daughter substances [9]. This will be discussed in detail elsewhere. Suffice it to say here that use of the stoichiometric amount of trimethylsilyl azide needed for acyl azide formation, rather than the large excess typically employed in earlier preparations, sharply depresses the side-reaction.

EXPERIMENTAL

X-ray diffraction analysis of **5**, *N*-azidocarbonyl-*N'*-nitro-3,5-diazahexacyclo[5.4.0.0^{2,6}.0^{2,10}.0^{6,9}.0^{8,11}]undecan-4-one, $C_{10}H_6N_6O_4$, FW = 274.2 has triclinic space group $P\bar{1}$, $a = 6.021(2)$, $b = 8.840(3)$, $c = 10.036(3)$ Å, $\alpha = 89.01(3)$, $\beta = 80.87(3)$, $\gamma = 87.65(3)^\circ$, $V = 527.0(3)$ Å^3, $Z = 2$, $D_{calc} = 1.728$ mg mm^{-3}, λ (CuKα) = 1.54184 Å, $\mu = 1.14$ mm^{-1}, $F_{000} = 280$, $T = 244$ K. In this section and in the Tables, numbers in parentheses represent the estimated standard deviation in the final digit of the reported parameter.

The clear colorless 0.07 x 0.20 x 0.40 mm lath-shaped crystal of **5** used for data collection was recrystallized from acetonitrile. Data were collected in the $\theta/2\theta$ scan mode with an automated Siemens R3*m*/V diffractometer equipped with an incident beam monochromator to $(\sin(\theta)/\lambda)_{max} = 0.531$ Å^{-1}. The range of *hkl* was: $-6 \leq h \leq 0$, $-9 \leq k \leq 9$, $-10 \leq l \leq 10$. Lattice parameters were determined from 25 centered reflections within $55 \leq 2\theta \leq 82^\circ$. The standards $00\bar{5}$, 040, 400, monitored after every 97 reflections, had a random variation of 2.0% over the data collection. The scan width varied from $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]^\circ$, and the ω scan rate was constant at 9.4° min^{-1}. A total of 1543 reflections were measured, 1336 unique with $R_{int} = 0.009$, and 1255 observed with $F_o > 3\sigma(F_o)$. Data were corrected for Lorentz and polarization effects. The structure solution, by direct methods, and the full-matrix least-squares refinement used programs in SHELXTL [10]. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, $g = 0.000225$, and the secondary extinction parameter in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$ was $p = 0.025(3)$. The 212 parameters refined include atomic coordinates for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. The largest shift to error ratio was $(\Delta/\sigma) = 0.002$, and the ratio of observations to parameters was 5.9:1. R factors were $R = 0.037$, $wR = 0.046$, $S = 1.99$ for the 1255 obs. data. $R = 0.039$ for all data. Final difference Fourier excursions were 0.19 and -0.19 e Å^{-3}. Atomic scattering factors are from International Tables for X-ray Crystallography [11]. Atom numbering for the bond distances and angles (Table 1), follows that shown in Figure 1. Table 2 contains atomic coordinates and thermal parameters for **5**.

Acknowledgement.

The work at The University of Chicago and also at the Naval Research Laboratory was supported in part by the Office of Naval Research, Mechanics Division.

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