with anhydrous magnesium sulfate, concentrated on a rotary evaporator, and purified by preparative TLC, eluting with ethyl acetate to give monodeuterated sulfoxide **7** ($X = D$) (90% D as determined by ^{1}H NMR spectroscopic analysis, 10, mg 52% yield): IR (KBr) 2170, 2042 (C–D) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (1 H, br dd, J = 13.5, 13.5 Hz, H_d), 2.21 (1 H, br d, J = 15.5 Hz, H_c) 2.49 (0.96 H, m, H_b), 2.64 (1 H, ddd, J = 4.1, 13.5, 13.5 Hz, H_e), 3.00 (1 H, br d, J = 13.1 Hz, H_f), 3.71 (0.13 H, ddd, J = 3.0, 12.9, 12.9 Hz, H_a), 7.49 (1 H, dd, J = 7.5, 7.5 Hz, H_k), 7.72 (1 H, dd, J = 7.7, 7.7 Hz, H_h), 7.87 (1 H, dd, J = 1.0, 7.0 Hz, H_l), 7.93 (1 H, dd, J = 7.7, 7.7 Hz, H_j), 7.95 (1 H, dd, J = 1.0, 8.3 Hz, H_i), 8.46 (1 H, dd, J = 1.0, 7.4 Hz, H_g).

Formation of Deuterated Dication 8 from Deuterated Sulfoxide 7 ($X = D$). A sample of monodeuterated sulfoxide **7** ($X = D$) (9.0 mg, 0.036 mmol) prepared as above was dissolved in ice-cold D_2SO_4 (95–97%, 1.5 mL). This red-brown solution was characterized as follows: ^{1}H NMR (D_2SO_4) δ 2.21 (1 H, m, $w_{1/2}$ = 0.14 ppm, H_c), 3.59 (1 H, br d, J = 14 Hz, H_d), 4.41 (1 H, br dd, J = 11.3, 11.3 Hz, H_b), 4.56 (2 H, br s, H_a), 8.06 (2 H, dd, J = 7.2, 7.2 Hz, H_{meta}), 8.47 (4 H, d, J = 7.6 Hz, H_{ortho}, H_{para}).

Hydrolysis of Deuterated Dication 8. After being allowed to stand at 0 °C for 15 min, the solution of deuterated dication **8** prepared as above was hydrolyzed in the same way as the undeuterated material to produce purified monodeuterated sulfoxide **7** (6.2 mg, 68% yield): ^{1}H NMR ($CDCl_3$) δ 1.58 (1 H, br dd, J = 15.5, 12.4 Hz, H_d), 2.23 (1 H, br dd, J = 15.5, 2.5 Hz, H_c), 2.54 (0.88 H, br d, J = 12.9 Hz, H_b), 2.61 (0.64 H, ddd, J = 12.4, 12.3, 4.1 Hz, H_e), 3.00 (0.88 H, br d, J = 12.3 Hz, H_f), 3.71 (0.68 H, ddd, J = 12.9, 12.4, 3.3 Hz, H_a), 7.47 (1 H, dd, J = 8.1, 7.1 Hz, H_k), 7.71 (1 H, dd, J = 8.1, 7.4 Hz, H_h), 7.86 (1 H, dd, J = 7.1, 1.2 Hz, H_l), 7.94 (1 H, dd, J = 8.1, 1.2 Hz, H_j), 7.95 (1 H, dd, J = 8.1, 1.2 Hz, H_i), 8.51 (1 H, dd, J = 7.4, 1.2 Hz, H_g).

Preparation of ^{18}O-Labeled Sulfoxide 7 ($X = H$). To a sample of naphtho[1,8-*bc*]-1,5-dithiocin (30.7 mg, 0.132 mmol) dissolved in glacial acetic acid (4 mL) was added ^{18}O-labeled water (97% ^{18}O, 150 μL) followed by the bromine complex of 1,4-diazabicyclo[2.2.2]octane[23] (50 mg, 0.12 mmol). After the reaction mixture was stirred at room temperature for 2 h, the solvent was removed under vacuum and dichloromethane (20 mL) was added. The mixture was filtered and the filtrate evaporated to a yellow oil on a rotary evaporator and purified by preparative TLC, eluting with ethyl acetate, to yield ^{18}O-labeled sulfoxide **7** ($X = H$) (22 mg, 77% yield): IR (KBr) 991, 968 (S–^{18}O) cm^{-1}; MS *m/e* $^{12}C_{13}{}^{32}S_2{}^{16}O$:$^{12}C_{13}{}^{32}S_2{}^{18}O$ ratio, 0.16:99.90.

Formation and Hydrolysis of Dication 8 from ^{18}O-Labeled Sulfoxide 7 ($X = H$). A sample of ^{18}O-labeled sulfoxide **7** ($X = H$) (11.4 mg, 0.046 mmol) was dissolved in ice-cold concentrated sulfuric acid (95–98%, 1.5 mL). The resulting red-brown solution was allowed to stand in an ice-water bath for 15 min and then it was added dropwise to a vigorously stirring ice-cold saturated aqueous solution of sodium bicarbonate (75 mL). The colorless aqueous solution was extracted with dichloromethane (3 × 100 mL). The extracts were combined, dried ($MgSO_4$), concentrated on a rotary evaporator, and purified by preparative TLC, eluting with ethyl acetate, to produce sulfoxide **7** ($X = H$) (8.7 mg, 77% yield): IR (KBr) 1024, 1007 (S–^{16}O) cm^{-1}; MS *m/e* $^{12}C_{13}{}^{32}S_2{}^{16}O$:$^{12}C_{13}{}^{32}S_2{}^{18}O$ ratio, 100:1.14.

Reaction of Sulfoxide 7 ($X = H$) with ^{18}O-Enriched Sulfuric Acid Followed by Hydrolysis. ^{18}O-Enriched sulfuric acid was prepared by slowly adding ^{18}O-labeled water (97% ^{18}O, 167 mg) to fuming sulfuric acid (18–24% SO_3, 1.748 g) with ice-water cooling. This material is 95–97% sulfuric acid with 10.6% ^{18}O enrichment. A sample of sulfoxide **7** ($X = H$) (13.6 mg, 0.055 mmol) was dissolved in the ^{18}O-enriched sulfuric acid (1.91 g) prepared as above with ice-water cooling. After allowing the red-brown mixture to stand at 0 °C for 15 min, it was added dropwise to a vigorously stirring ice-cold saturated aqueous solution of sodium bicarbonate (100 mL). The mixture was worked up as before to afford sulfoxide **7** ($X = H$) (9.4 mg, 70% yield) after purification: IR (KBr) 1024, 1007 (S–^{16}O) cm^{-1}; MS *m/e* $^{12}C_{13}{}^{32}S_2{}^{16}O$:$^{12}C_{13}{}^{32}S_2{}^{18}O$ ratio, 100:0.13.

Acknowledgment. We acknowledge support of this work by the U.S. Public Health Service, National Institute of Health, Grant No. HL 15104. The crystal structure of sulfoxide 7 (X = H) was determined at the Molecular Structure Laboratory of the University of Arizona. Helpful discussions with Professor W. K. Musker of the University of California, Davis, on the mechanism of formation and hydrolysis of dication 8 are gratefully acknowledged.

Supplementary Material Available: Stereoscopic view of sulfoxide **7** ($X = H$) and the packing of the molecules in the unit cell and tables of final atomic positional and thermal parameters, bond lengths, bond angles, and selected torsion angle data (8 pages) (a listing of structure factor amplitudes is available from the authors). Ordering information is given on any current masthead page.

Cubanourea: A Cubane-Propellane

Philip E. Eaton* and Kakumanu Pramod

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Richard Gilardi

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375

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Reaction of 1,2-diisocyanatocubane with limited amounts of water gives a propellane (**2**) in which a urea is fused to an edge of cubane. A suggestion for the unexpectedly ready formation of this new, strained ring system is given along with some of its chemistry. The structure of **2**, determined by X-ray crystallography, is discussed in comparison of those of other ureas. Nitration of **2** gives the high-energy bisnitramine derivative, whose detailed structure is established by X-ray analysis.

Excellent methodology has been developed for the preparation of variously substituted cubanes.[1] This allows us to start with the cubane system, already an extraordinary structure, and move further in our continuing exploration of highly strained systems.[2] We report now on the synthesis and structure of a cubane derivative wherein

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[1] (a) Eaton, P. E.; Castaldi, G. J. *J. Am. Chem. Soc.* **1985**, *107*, 724. (b) Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *Ibid.* **1987**, *109*, 948. (c) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055. (d) Eaton, P. E.; Cunkle, G. T. *Ibid.* **1986**, *27*, 6055.

[2] (a) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189. (b) Eaton, P. E.; Hormann, R. E. *J. Am. Chem. Soc.* **1987**, *109*, 1268. (c) Eaton, P. E.; Hoffmann, K.-L. *Ibid.* **1987**, *109*, 5285. (d) Eaton, P. E.; Maggini, M. *Ibid.* **1988**, *110*, 7230. (e) Eaton, P. E. Tsanaktsidis, J. *Ibid.* **1990**, *112*, 876.

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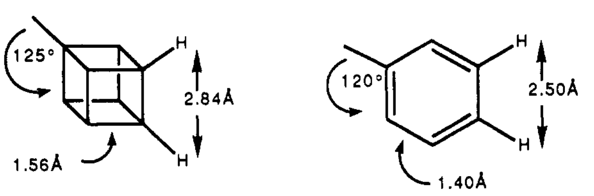
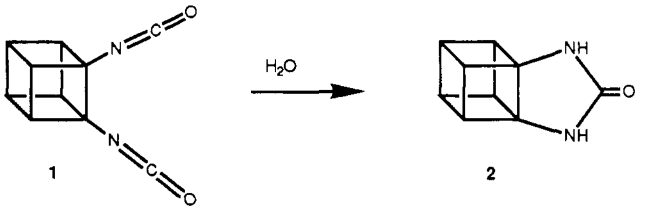


Figure 1. Calculated distances and angles in cubane and benzene.

a urea and a cubane share a common bond. This very highly strained material, colloquially "cubanourea", is a hetero[3.2.2]propellane.

The geometry of cubane is such that substituents on adjacent positions are further removed from one another than those ortho on an aromatic ring. The key differences between the geometry of the two systems are the longer carbon–carbon bond in cubane (1.56 Å vs 1.40 Å)[3] and the wider angle of this bond with an attached substituent (125° vs 120°). Thus, the distance between the adjacent "ortho" hydrogens is more than 0.3 Å longer in cubane than in benzene (Figure 1; note that each HCCH subunit is planar in both structures). The effect is magnified with substituents other than hydrogen whose attachment to the skeleton is through bonds longer than that of the typical CH length of 1.10 Å. As a consequence, through-space interactions between adjacent groups on the cubane frame are not as pronounced as they are in the benzene analogues. It was not surprising therefore to find that hydrolysis of cubane carboxamides is not noticeably enhanced by an adjacent carboxyl group, whereas it is well-known that 2-carboxybenzamides undergo ready hydrolysis because of such internal assistance.[4] Similarly, although phthalic anhydride forms easily from o-phthalic acid, we have not been able to dehydrate cubane-1,2-dicarboxylic acid to an isolable monomeric anhydride. Reaction with ethoxyacetylene gives material which shows no substantial infrared absorptions in the 1670–1870 cm^{-1} region that might indicate the formation of a strained 5-membered anhydride; the principal products appear to be polymeric anhydrides.[5]

In the course of our work with cubane-1,2-dicarboxylic acid[6] we prepared in good yield (see the Experimental Section) the 1,2-diisocyanate **1**, a stable crystalline solid of substantial interest as a monomer for novel polyurethanes. Hydrolysis of **1** with 3 N hydrochloric acid gives 1,2-diaminocubane bishydrochloride in excellent yield, but reaction in dilute solution in acetone with a minimum amount of water produces the cubanourea **2** in 51% yield. Given the comments just made about the geometry of cubane, this is exceedingly surprising.[7]



1 **2**

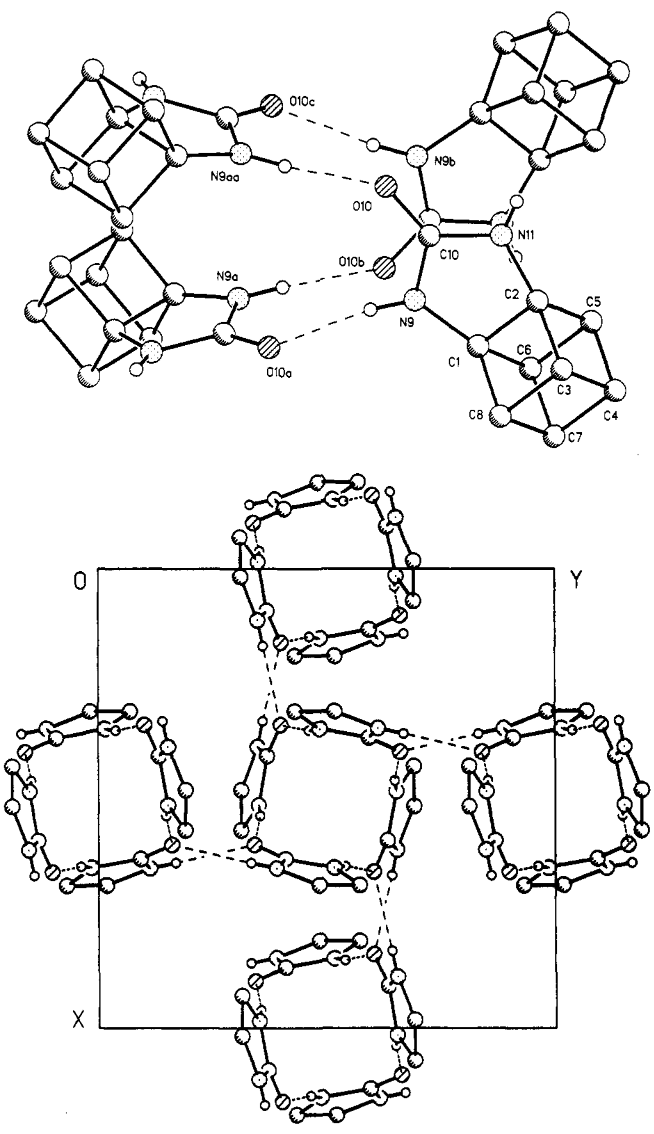


Figure 2. (a, top) A view of a tetramer of cubanourea, strongly bound by linear [N–H···O] H-bonds. The 4-fold axis which relates these molecules is horizontal in this view and runs through the center of the tetramer. (b, bottom) A view emphasizing the extensive system of H-bond linkages involved in the packing of the cubanourea molecules. (The cubane portions of the molecules have been omitted for clarity.) The central tetramer is linked to four others; those at the top and bottom are ca. 5 Å further, those at left and right ca. 5 Å closer, than the central one. (Thre is also a tetramer at each corner of the cell, at still another level in height.)

Cubanourea is the first hetero fused-ring cubane to be made and identified. Its structure was established initially from spectral information, most particularly the NMR data which clearly demonstrate the molecule has mirror plane symmetry. Single-crystal X-ray analysis confirmed the structural assignment fully. Asymmetrical packing contacts lead to slight, insignificant deviations from exact mirror symmetry in the crystal.

The packing arrangement of molecules in **2** is complicated. Two types of linear hydrogen bonds are formed, corresponding to the two independent amido hydrogens in the molecule. H-bonds involving H9 [e.g., N9–H9···O10 at 1−y,x,−z] link molecules into tetramers with the units related by the crystallographic 4-fold inversion axis (Figure 2a). Each of these tetramers is linked to four others by

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[3] (a) These values are those of MMX calculations using PCMODEL (Serena Software, Bloomington Indiana).

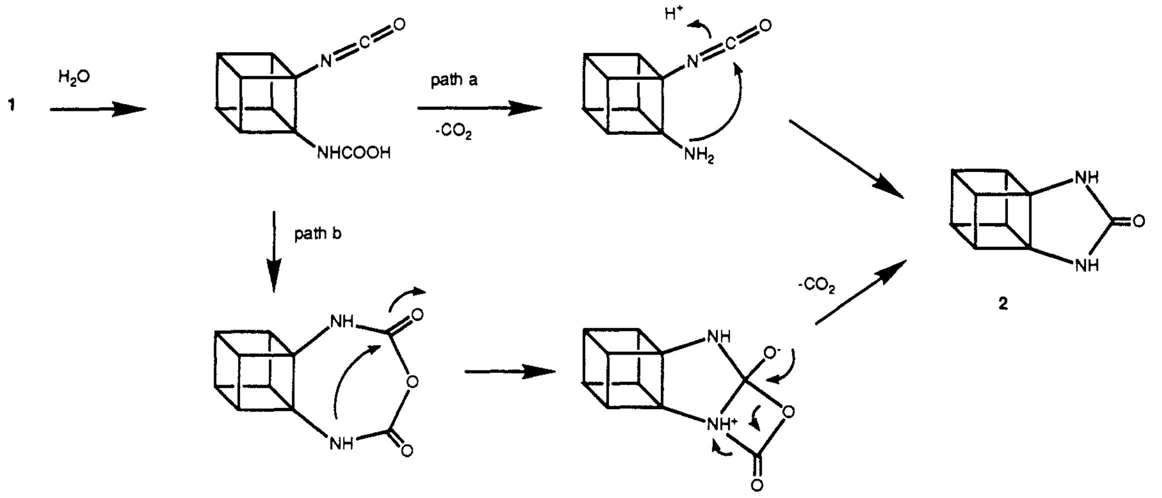
[4] Nonetheless, there are significant, if less well-defined interactions between adjacent cubane substituents: viz. the stabilization of electropositive metal salts by adjacent amido groups.[1a]

[5] In the course of one such experiment we heated the crude anhydride mixture under high vacuum hoping to collect whatever "volatile" monomeric anhydride was present. The mixture exploded violently at 80 °C. This is entirely atypical of simple cubanes.

[6] Eaton, P. E.; Bashir-Hashemi, A.; Pramod, K.; Chou, C. T., unpublished results.

[7] o-Tolylene-1,2-diisocyanate reacts easily with water to give the cyclic urea. See: Schnabel, W. J.; Kober, E. J. Org. Chem. 1969, 34, 1162.

Scheme I

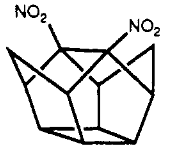


H-bonds involving H11 [e.g., N11-H1···O10 at x, $1/2-y$, $1/4-z$]. These linkages are repeated by lattice symmetry in all directions, so that each molecule is connected, directly or indirectly, to every other molecule in the crystal (Figure 2b). The high melting point of **2** (220 °C dec) follows as a consequence of this extensive cross-linking.

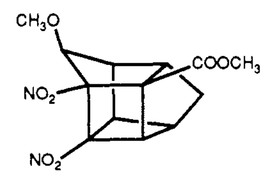
The most interesting features of the molecular structure of cubanourea are (1) the length of the bond C1–C2 shared by the urea ring and the cubane frame is substantially shorter [1.526 (3) Å] than that in cubane [1.551 (3) Å],[8] in any other cubane structure reported to date, or in comparable (saturated, 5-membered) ureas (range: 1.547–1.580 Å, av 1.566 Å);[9] (2) the angle between the shared bond and the cubyl C–N bond is significantly contracted [104.4 (2)° and 103.9 (2)°] from the 125° CCH angle of cubane but is not far from those seen in comparable ureas (range: 100.8–103.5°, av 102.2°);[9] (3) the cubyl C–N bond length [1.418 (3) and 1.425 (3) Å] is shortened relative to those in comparable ureas (range: 1.428–1.485 Å,[9] av 1.454 Å).

Although we had previously thought of cubane as a "hard", inflexible system, it is apparently rather "soft", capable of substantial distortions. To a degree, distortions of type 2 and 3 above are synergistic; both can be understood in terms of enhanced s character (31%) in the exocyclic orbitals of cubanes.[10] Angular force constants are expected to be lower for such less directed orbitals. However, the shortening of the shared C1–C2 bond, a bond formed from p-rich orbitals, runs counter to this argument, and would seem to heighten the strain in the system. Because of this "discrepancy", our initial determination, which was quite respectable [d = 1.524 (4) Å, Cu Kα X-rays, R = 0.035 for 766 observed data], was repeated using another crystal and conditions which led to more (1594) and better (less absorption) data. The two sets of results were not significantly different.

Why then is the C1–C2 bond shortened? We find no satisfaction in the possible argument that bonds connecting carbons carrying two electronegative substituents should be short,[11] particularly when there are steric (strain) forces to contend with. Indeed, in the vicinal dinitro bishomopentaprismane **3**, reported by Paquette et al.,[12] the *longest* C–C bond is between those carbons bearing the strongly electronegative nitro groups. In the *vic*-dinitrobishomocubane derivative **4**, reported by Marchand and co-workers,[13] the bond between the nitrated carbons (now part of a cyclobutane ring) is quite short (1.522 (5) Å), but there are C–C bonds both longer and shorter in the molecule, belying any easy conclusion. The answer to the question must wait for the determination of the structural details of more 1,2-disubstituted cubanes.



3



4

We do not know the detailed mechanism for the formation of cubanourea from the diisocyanate. A variety of different paths can be conceived. Two are shown in Scheme I. The direct 5-membered ring closure step in path a seems unlikely, considering the long distance between the free amine and the rigid linear isocyanate group. At this point we favor the alternative path b in which a relatively large ring is closed first, and this subsequently undergoes an intramolecular contraction driven by loss of carbon dioxide.

Like most most ureas, cubanourea is very resistant to basic hydrolysis, surviving quite vigorous treatment. Apparently the mechanism of alkaline hydrolysis is not aided by the relief of strain which would accompany the ring

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(8) Fleischer, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3889.

(9) The values given as typical bond distances for angles for "comparable ureas" come from nine articles containing 16 independent X-ray analyses of C-substituted 2-imidazolidones, obtained by using the Cambridge Structural Database and its search software, as described in Allen, F. H.; Bellard, S. A.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rogers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331. The citations are: (a) Glick, M. D.; Wormser, H. C.; Abramson, H. N. *Acta Crystallogr.* **1977**, *33*, 1095. (b) Paton, W. F.; Liu, F.-T.; Paul, I. C. *J. Am. Chem. Soc.* **1979**, *101*, 1005. (c) DeTitta, G. T.; Edmonds, J. W.; Stallings, W.; Donohue, J. *J. Am. Chem. Soc.* **1976**, *98*, 1920. (d) DeTitta, G. T.; Parthasarathy, R.; Blessing, R. H.; Stallings, W. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 333. (e) Rapi, G.; Chelli, M.; Ginanneschi, M. Donati, D.; Selva, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1339. (f) Hannick, S. M.; Kishi, Y. *J. Org. Chem.* **1983**, *48*, 3833. (g) Chen, C.-S.; Parthasarathy, R.; DeTitta, G. T. *J. Am. Chem. Soc.* **1976**, *98*, 4983. (h) Himes, V. L.; Hubbard, C. R.; Mighell, A. D.; Fatiadi, A. J. *Acta Crystallogr.* **1978**, *34*, 3102. (i) Jacobi, P. A.; Brownstein, A.; Martinelli, M.; Grozinger, K. *J. Am. Chem. Soc.* **1981**, *103*, 239.

(10) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.

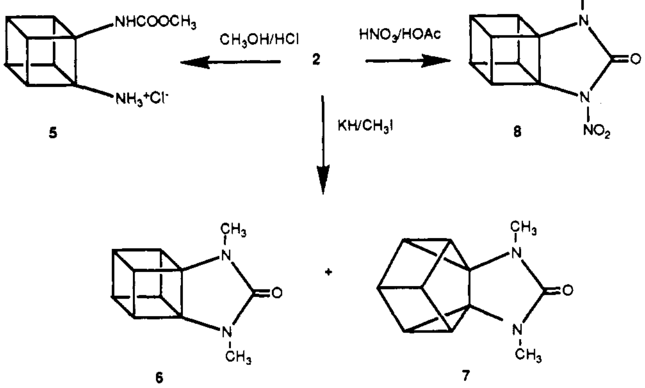
(11) See the discussion in Bent, H. A. *Chem. Rev.* **1961**, *61*, 275–311.

(12) Paquette, L. A.; Fischer, J. W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524.

(13) Marchand, A. P.; Jin, P.-W.; Flippen-Anderson, J. L.; Gilardi, R.; George, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1108.

opening. Acid hydrolysis also proceeds at a rate not dissimilar to that of simple ureas. Reaction with methanolic hydrogen chloride gives **5**, the hydrochloride of the 1,2-aminocarbamate. N,N′-Alkylation of **2** with methyl iodide and potassium hydride in THF gives **6** as well as the related[14] cuneane **7** in about equal amounts. It is not yet clear at what point the cuneane arises; preliminary evidence favors rearrangement of the anion of monoalkylated **2**. We shall report on additional work in this area in due course.

N,N′-Dinitration of **2** is effected readily with anhydrous nitric acid in acetic anhydride and proceeds in good yield without the formation of a cuneane.[15] Single-crystal X-ray analysis (see the supplementary material) was used to confirm the structure of the bisnitramine **8** so produced. Again, the C–C bond between the electronegatively substituted carbons of the cubane portion is short [1.534 (3) Å], but even with the large increase in the electron-withdrawing capacity of the substituents the bond is slightly longer than it is in urea **2**. For comparison purposes it should be noted that the C–C bond in *N*,*N*′-dinitro-1,3-diazacyclopentan-2-one is 1.527 (4) Å.[16]



Whether or not the formation and stability of cubanourea are simply entropy-driven flukes or are related to an important structural interaction between the electronic structure of the urea and the p-rich orbitals of the cubane carbon–carbon bonds is not clear at this stage. We shall report on this aspect as we obtain further information. Presently we are looking to take cubane-1,2,4,7-tetracarboxylic acid[1c] to a cubanobisurea in which two hetero rings are fused on opposite edges of cubane.

Experimental Section

NMR spectra were run in chloroform-*d* unless otherwise noted: ^{1}H NMR at 400 MHz and referenced to internal tetramethylsilane (0.00 ppm); ^{13}C NMR at 100 MHz and referenced to the central line of the solvent. Proton chemical shifts are reported to a precision of ±0.02 ppm; carbon chemical shifts are reported to ±0.1 ppm. Mass spectra are electron-impact spectra. Infrared spectra were recorded at 1 cm^{-1} resolution.

1,2-Diisocyanatocubane (1). Oxalyl chloride (5 mL) was added to solid cubane-1,2-dicarboxylic acid (0.96 g, 5.0 mmol) under inert atmosphere, and the mixture heated in an oil bath with stirring at reflux until it became homogeneous (3–4 h). The mixture was cooled; excess oxalyl chloride was removed under reduced pressure at room temperature, leaving the crude diacid chloride as a crystalline solid. Traces of oxalyl chloride trapped in the solid were removed by pumping under high vacuum for 1 h. Trimethylsilyl azide (Aldrich, 2.6 mL, 20 mmol) in dry benzene (5 mL) was added, and the mixture was stirred at room temperature for 2 h. *Caution: At this point the solution contains the potentially explosive cubane-1,2-diacylazide. Do not evaporate to dryness*! The solution was then diluted with dry benzene (70 mL) and refluxed (to effect rearrangement) with stirring until evolution of gas ceased. The solvent was evaporated under reduced pressure, giving crude **1** as a crystalline solid (855 mg, 92%). It was purified by sublimation at 65 °C (0.1 Torr): mp 142–144 °C dec; IR (KBr) ν 2265, 1226 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.03 (m, 4 H), 3.86 ppm (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 124.5, 69.4, 50.7, 43.4 ppm; *m/e* 186.0438 (P$^+$, calcd 186.0429).

3,5-Diazahexacyclo[5.4.0.0^{2,6}.0^{2,10}.0^{6,9}.0^{8,11}]undecan-4-one (Cubanourea, 2). 1,2-Diisocyanatocubane (830 mg) in dry THF (40 mL) was added dropwise to a stirred solution of wet (0.5 mL of water) acetone (500 mL) at room temperature over a period of 12 h using a motor-driven syringe pump. The reaction mixture was stirred for 20 h more and then concentrated under reduced pressure. The brownish residue was chromatographed on silica gel (Merck, grade 60, 230–400 mesh) with 1:1 CHCl$_3$–EtOAc. Evaporation of the later fractions under reduced pressure gave a white crystalline solid (410 mg, 51%). Crystallization from methanol gave square bipyramids: mp 220 °C dec; IR (KBr) ν 3221, 1684 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.5 (br, 2 H), 4.30 (m, 4 H), 3.83 ppm (m, 2 H); ^{13}C NMR (CD$_3$OD) δ 167.9, 68.2, 58.2, 43.4 ppm; *m/e* 160 (P$^+$, 5). Anal. Calcd for C$_9$H$_8$N$_2$O: C, 67.48; H, 5.03; N, 17.48. Found: C, 67.29; H, 5.00; N, 17.22.

Single-crystal X-ray diffraction analysis of 3,5-diazahexacyclo[5.4.0.0^{2,6}.0^{2,10}.0^{6,9}.0^{8,11}]undecan-4-one (2): C$_9$H$_8$N$_2$O, FW = 160.2; tetragonal space group $I\bar{4}2d$; a = 12.304 (2), c = 19.850 (4) Å; vol. = 3005.2 (1.1) Å^3; Z = 16; ρ_{calc} = 1.416 g/cm^3; λ(Mo Kα) = 0.710 73 Å; μ = 0.90 cm^{-1}; F(000) = 1344; T = 295 K.

A clear colorless 0.15 × 0.15 × 0.12 mm crystal, shaped like a tetragonal bipyramid, was used for data collection on an automated Nicolet R3m/V diffractometer with an incident beam monochromator. Lattice parameters were determined from 44 centered reflections within $31 \leq 2\theta \leq 40°$ and $-40 \leq 2\theta \leq -31°$. The data collection range of *hkl* was: $-16 \leq h \leq 16$, $0 \leq k \leq 16$, $-25 \leq l \leq 25$, $(\sin(\theta/\lambda))_{\max} = 0.6497$ Å^{-1}. Three standards, monitored every 60 reflections, exhibited a maximum random variation of 3.5% during data collection. A highly redundant set of 7378 reflections was collected in the $\theta/2\theta$ scan mode with a constant 2θ scan rate of 10 deg/min. There were 1751 *unique* reflections, and 1594 were observed with $F_o > 3\sigma(F_o)$. The structure was solved and refined with the aid of the SHELXTL system of programs.[17] The full-matrix least-squares refinement varied 196 parameters: atom coordinates, anisotropic thermal parameters for all non-H atoms, and isotropic thermal parameters for the hydrogens. Final residuals were R = 0.058 and R_w = 0.049 with final difference Fourier excursions of 0.41 and −0.35 e Å^{-3}.

Acid Hydrolysis of Cubanourea To Give 5. Cubanourea **2** (20 mg, 0.125 mmol) was stirred with a dilute solution of methanolic HCl (3 mL) at room temperature for 14 h. The volatiles were removed under reduced pressure; the gummy residue was dried in vacuo (28 mg, ~100%). The material is not stable in air at room temperature, but is stable for days cold under nitrogen: IR (neat) ν 3210, 2999, 2956, 1697, 1518, 1459, 1343, 1292, 1267, 1062 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ 4.12 (m, 2 H), 4.08 (m, 2 H), 3.96 (m, 1 H), 3.89 (m, 1 H), 3.68 ppm (s, 3 H); ^{13}C NMR (CD$_3$OD) δ 158.4, 70.0, 69.5, 52.8, 49.7, 47.5, 45.1, 44.9 ppm.; *m/e* 192 (P$^+$ − HCl).

3,5-Dimethyl-3,5-diazahexacyclo[5.4.0.0^{2,6}.0^{2,10}.0^{6,9}.0^{8,11}]undecan-4-one (6) and 2,4-Dimethyl-2,4-diazahexacyclo[3.3.3.0^{1,5}.0^{5,6}.0^{7,10}.0^{8,11}]undecan-3-one (7). A solution of cubanourea **2** (80 mg, 0.5 mmol) in dry THF (2 mL) was added to a stirred suspension of potassium hydride (100 mg, 2.5 mmol) in THF (5 mL) at 0 °C. The mixture was heated to 50 °C for 30 min and then recooled to 0 °C. Methyl iodide (1 mL) was added, and the whole was stirred at 50–55 °C for 14 h. It was then cooled. Excess KH was quenched by dropwise addition of methanol. The whole was poured into water and extracted with ether (3 × 10 mL). The extract was washed with water and brine and then dried

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(Na_2SO_4). Evaporation of the solvent left a pale yellow residue (110 mg). This was chromatographed on silica gel with ether–pentane (1:1), giving first the cubane **6** (37 mg, 39%) and then the cuneane **7** (32 mg, 34%). **6**: mp 112–113 °C; IR (KBr) ν 2991, 2982, 2938, 1695, 1415, 1383, 1093, 1041, 750, 569 cm^{-1}; ^1H NMR δ 4.34 (m, 4 H), 3.88 (m, 2 H), 2.79 ppm (s, 6 H); ^{13}C NMR δ 162.5, 67.8, 54.8, 42.6, 27.5 ppm; *m/e* 188 (P^+, 80), 162 (100). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42; N, 14.88. Found: C, 70.11; H, 6.47; N, 14.72. **7**: mp 78–79 °C; IR (KBr) ν 3043, 3011, 2923, 1699, 1684, 1427, 1377, 1087, 923, 809, 750, 574, 467 cm^{-1}; ^1H NMR δ 3.07 (m, 2 H), 2.77 (s, 6 H), 2.63 ppm (m, 4 H); ^{13}c NMR δ 161.5 (s), 67.8 (s), 46.2 (d, J = 154 Hz), 3.16 (d, J = 180 Hz), 28.1 (q) ppm; *m/e* 188 (P^+, 10), 162 (100). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42; N, 14.88. Found: C, 70.08; H, 6.31; N, 14.75.

3,5-Dinitro-3,5-diazahexacyclo[5.4.0.$0^{2,6}$.$0^{2,10}$.$0^{6,9}$.$0^{8,11}$]undecan-4-one (8). 100% Nitric acid (315 mg, 5.00 mmol)[14] was injected dropwise into a stirred solution of dry CH_2Cl_2 (3 mL) and acetic anhydride (510 mg, 5.00 mmol) at 0 °C under argon. After 30 min at 0 °C, the reaction mixture was allowed to warm to room temperature and then recooled to 0 °C. Powdered cubanourea **2** (65 mg, 0.41 mmol) solid was added all at once; stirring was continued at 0 °C for 2 h. Crushed ice was then added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to give fine crystalline needles of **8** (83 mg, 82%): mp 210 °C dec, IR (KBr) ν 1802, 1573, 1310, 1160, 1140, 1015, 883, 729, 699 cm^{-1}; UV (CH_3CN) λ_{max} 279 nm (ϵ 5500); ^1H NMR δ 4.69 (m, 4 H), 4.19 ppm (m, 2 H); ^{13}C NMR δ 141.2, 63.1, 54.9, 43.6 ppm. Anal. Calcd for $C_9H_6N_4O_5$: C, 43.21; H, 2.41; N, 22.39. Found: C, 43.,07; H, 2.27; N, 22.13.

Single-crystal X-ray diffraction analysis of 3,5-dinitro-3,5-diazahexacyclo[5.4.0.$0^{2,6}$.$0^{2,10}$.$0^{6,9}$.$0^{8,11}$]undecan-4-one: $C_9H_6N_4O_5$, FW = 250.2; monoclinic space group $P2_1/c$; a = 9.669 (3), b = 5.972 (1), c = 16.584 (6) Å; β = 91.12 (3)°; vol. = 957.3 (5) $Å^3$; Z = 4; ρ_{calc} = 1.736 g/cm^3; λ(Mo Kα) = 0.71073 Å; μ = 1.36 cm^{-1}; F(000) = 512, T = 295 K.

A clear colorless 0.10 × 0.20 × 0.45 mm crystal, shaped like a rectangular prism, was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator. Lattice parameters were determined from 30 centered reflections within $20 \leq 2\theta \leq 30°$. The data collection range of *hkl* was: $0 \leq h \leq 10$, $-6 \leq k \leq 0$, $-17 \leq l \leq 17$, $(\sin(\theta)/\lambda)_{max}$ = 0.5384 $Å^{-1}$. Three standards were monitored every 60 reflections and exhibited a maximum random variation of 2.0% during data collection. A total of 1562 reflections were measured in the $\theta/2\theta$ mode with a variable 2θ scan rate, ranging from 10.0 to 31.2 deg/min. There were 1262 *unique* reflections, and 1121 were observed with $F_o > 3\sigma(F_o)$. The structure was solved by direct methods with the aid of program SHELXTL.[17] The full-matrix least-squares refinement varied 188 parameters: atom coordinates, anisotropic thermal parameters for all non-H atoms, and isotropic thermal parameters for the hydrogens. Final residuals were R = 0.034 and R_w = 0.041 with final difference Fourier excursions of 0.17 and −0.23 e $Å^{-3}$.

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Registry No. 1, 129103-49-7; 2, 129103-50-0; 5, 129103-52-2; 6, 129103-53-3; 7, 129103-54-4; 8, 129103-55-5; cubane-1,2-dicarboxylic acid, 129103-51-1.

Supplementary Material Available: ^{13}C NMR spectra of compounds **1** and **5**; numbered ORTEP drawings of compounds **2** and **8**; tables of atomic position parameters, Cartesian coordinates, bond distances, bond angles, torsion angles, and anisotropic thermal parameters for both X-ray structures (11 pages); tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Photochemistry of Functionalized Diphosphiranes

Maryse Gouygou, Christine Tachon, and Max Koenig*

URA 454, Université Paul Sabatier, 31062 Toulouse Cedex, France

Antoine Dubourg

Faculté de Pharmacie, Avenue Charles Flahaut, 34060 Montpellier, France

Jean-Paul Declercq

Université Catholique de Louvain, 1, Place L. Pasteur, B-1348 Louvain-La-Neuve, Belgium

Joël Jaud and Guita Etemad-Moghadam

Laboratoire de Chimie de Coordination du CNRS, 205, Route de Narbonne, 31077 Toulouse Cedex, France

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The structure of the functionalized *trans*-diphosphiranes **1a–e**, obtained by reaction of halogenocarbenes with the *trans*-diphosphene is confirmed by X-ray diffraction. The photolysis of **1a–e** lead to the functionalized *cis*- and *trans*-1,3-diphosphapropenes **2a–e** as major products, via the diphosphiranyl **7** and the diphosphapropenyl **8** radical intermediates. The latter are characterized by ESR spectroscopy using the spin–trap method. The trans configuration of **2a** is also confirmed by X-ray diffraction. The mechanism of the ring-opening, involving P–P bond rupture, is discussed.

Whereas *gem*-dihalocyclopropanes are known to undergo thermally promoted skeletal rearrangements to 1,2-dihaloprop-2-ene derivatives[1] (Figure 1, reaction A), their photochemistry is different. For example, the irradiation of *gem*-dichloroarylcyclopropanes with UV light produces a dichlorocarbene (Figure 1, reaction B),[2] characteristic of reactions analogous to the photochemical fragmentation

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