

The Crystal Structure of 1,3,5-Triphenyl-1,3,5-perhydrotriazine-2,4,6-trione (Phenylisocyanurate)

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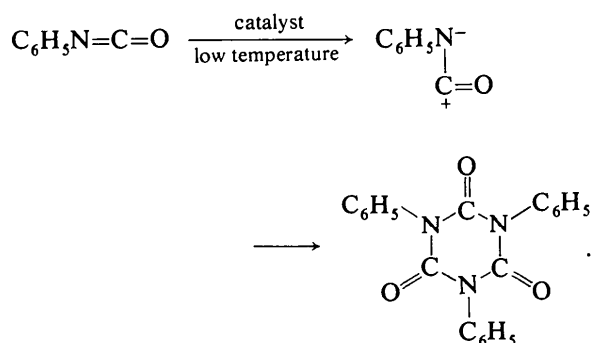
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Abstract

$C_{21}H_{15}N_3O_3$ is monoclinic, space group $C2/c$, with $a = 16.342$ (70), $b = 13.797$ (4), $c = 9.855$ (5) Å, $\beta = 129.08$ (2)°, $Z = 4$. Refinement based on 1343 reflections led to $R = 0.049$. The molecules form a layer-like structure with the cyanuric rings parallel. The benzene rings make angles of 72.9° with the cyanuric ring.

Introduction

The self-condensation of phenyl isocyanate to yield the trimer has long been known (Saunders & Slocombe, 1948). The reaction of the monomer to form the cyclic trimer is catalysed by complex metal hydrates (Ellzey & Mack, 1963), tertiary amines (Beitchman, 1966) and *N*-methylmorpholine (Kogan, 1956). Shashoua, Sweeny & Tietz (1960) reported the self-condensation of the monomer to a polymer at low temperatures (195 K) and to the trimer at high temperatures (398 K) by anionic catalysts. Natta, DiPietro & Cambini (1962) reported that a highly crystalline polymer could be obtained at low temperature with organometallic catalysts. In this work, it is shown that the trimer can be obtained in high yield at low temperature with a suitable catalyst concentration. The equation of the reaction is



The structure of phenylisocyanurate has not previously been determined. However, Brown (1955)

reported that its crystal is monoclinic, space group Ia or $I2/a$, with $a = 12.67$, $b = 13.76$, $c = 9.83$ Å, $\beta = 90^\circ$. Similar structures such as cyanuric acid (Wiebenga, 1952) and melamine (Hughes, 1941) have been reported.

The present work confirms the data reported by Brown. However, in our case $\beta = 92.7^\circ$.

Experimental

(i) Preparation of phenylisocyanurate

Phenyl isocyanate obtained from Eastman Kodak was dried over $CaCl_2$ and purified by triple distillation at 26.7×10^2 Pa and 323 K. The boiling point was 438.3 ± 0.2 K and the specific gravity 1.08.

Trimerization of phenyl isocyanate was carried out in a 100 ml Pyrex glass tube, equipped with a side arm. The tube was flamed while being swept with dry helium in order to ensure maximum dryness. The helium was purified and dried with a train of alkaline pyrogallol, concentrated sulfuric acid, KOH, $CaCl_2$ and a CO_2 absorbent produced by the Fisher Scientific Co., before reaching the reaction tube. Carbon disulfide (20 ml) was added to the tube, followed by phenyl isocyanate (25 ml). The contents were cooled to 195 K in dry ice-acetone. With a syringe, 1.0 ml of the catalyst, ethyllithium in benzene (0.25%), was rapidly added to the system, while a stream of helium was continuously sweeping over it. The reaction product, a mixture of a white powder and needle-like single crystals, was washed with 5% HCl solution and dried at 323 K under vacuum. The yield was about 91%. Similar products with a yield of 80–90% were obtained with benzene, THF, DMF, CH_2Cl_2 and acetone as solvents. When toluene was used, 2% of a gel-type product was obtained.

The trimerization did not take place with NaCN as catalyst. However, when raised to room temperature, the reaction was exothermic and the product, a fine crystalline material, gave two sharp IR peaks at 5.89 and 6.00 μm . A similar product was obtained from the decomposition of phenylisocyanurate at its melting

point, 553–555 K. Chemical analysis gave 70.75% C, 13.62% O, 11.91% N and 4.57% H, similar to the calculated values.

The molecular weight was determined ebullioscopically. The result was 430, 344 and 358 with chloroform, pyridine and acetonitrile as solvent, respectively. The calculated molecular weight is 358. The density obtained by flotation in aqueous AgNO_3 was 1.34 Mg m^{-3} . The IR spectrum showed an intense peak at $5.89 \mu\text{m}$ due to the C=O group.

(ii) Crystal-data collection

The space group and approximate cell parameters were obtained from precession and Weissenberg photographs. Systematic absences (hkl with $h + k + l = \text{odd}$, $h0l$ with $h = \text{odd}$, $l = \text{odd}$) showed the space group to be Ia or $I2/a$.

Intensities were collected on a Picker diffractometer (equipped with a Cu tube and scintillation counter) by the θ - 2θ scan method. Precise cell parameters were determined by least squares from 12 reflections which were automatically centered and well distributed in reciprocal space. The cell parameters were $a = 16.342$ (70), $b = 13.797$ (4), $c = 9.855$ (5) Å, $\beta = 129.08$ (2)°, after converting the body-centered cell to a centered cell with the transformation matrix 101/010/001 for hkl . The space group in this case is either Cc or $C2/c$. d_x for $Z = 4$ is 1.38; d_o was 1.34 Mg m^{-3} .

The needle axis of the crystal was chosen as c . The other faces of the crystal were bounded by [011]

planes. The crystal used for intensity collection was $0.2 \times 0.2 \times 0.4 \text{ mm}$.

From the permitted 1369 reflections with $5 < 2\theta < 125^\circ$, 1360 unique reflections were observed. Background was counted on each side of the peak for 10 s with stationary crystal and detector. The scan range was 3° .

Solution of the structure

The intensities were corrected for background and Lorentz-polarization factors. The temperature and scale factors were calculated from a Wilson (1942) plot with a program written by Bernstein (1973). The overall temperature factor was $B = 3.105 \text{ \AA}^2$. The distribution of intensities suggested centrosymmetry and the structure was solved in $C2/c$ by direct methods (Long, 1965).

The function minimized in the least-squares refinement was $\sum w|F_o^2 - |F_c|^2|^2$, where $w = 1/\sigma^2(F_o)^2$ with $\sigma^2(F_o)^2 = \sigma_{\text{count}}^2(F_o)^2 + (0.05 F_o^2)^2$ and σ_{count}^2 is based on counting statistics. R reduced to 0.17 with isotropic and to 0.11 with anisotropic temperature factors.

Seven of the eight H atoms were located from a difference map. Seventeen reflections affected by extinction were removed from the calculations. The remaining H atom was then located from a difference map. The final $R = 0.049$ and $R_w = 0.069$.*

Fractional coordinates are listed in Table 1.

Table 1. Fractional coordinates ($\times 10^5$; $\times 10^3$ for H atoms) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	50000	-15307 (11)	25000
O(2)	34173 (9)	13113 (9)	19294 (19)
N(1)	50000	13523 (13)	25000
N(2)	41436 (9)	-1214 (10)	20458 (16)
C(1)	50000	-6678 (15)	25000
C(2)	41319 (11)	8828 (12)	21533 (20)
C(3)	50000	24062 (15)	25000
C(4)	6840 (15)	-21064 (13)	40624 (26)
C(5)	6791 (16)	-10981 (15)	40425 (32)
C(6)	0	-6048 (20)	25000
C(7)	32096 (11)	-6569 (11)	14778 (19)
C(8)	25440 (14)	10251 (12)	48072 (22)
C(9)	16631 (15)	15546 (14)	42843 (27)
C(10)	14643 (15)	-16956 (14)	4258 (13)
C(11)	21267 (18)	-13218 (16)	20908 (32)
C(12)	30125 (14)	-8018 (14)	36306 (23)
H(1)	381 (2)	-251 (2)	481 (3)
H(2)	117 (2)	-75 (2)	521 (4)
H(3)	0	-1 (3)	250
H(4)	272 (2)	91 (2)	408 (3)
H(5)	126 (2)	188 (2)	312 (4)
H(6)	87 (2)	-211 (2)	6 (3)
H(7)	196 (2)	-145 (2)	283 (3)
H(8)	350 (2)	-52 (2)	380 (3)

Description of the structure

The structure is illustrated in Fig. 1 (Johnson, 1965). The cyanuric ring is almost planar; the equation of the least-squares plane passing through C(2), O(2) and N(2) is $3.321x + 9.731y - 8.734z + 0.423 = 0$. Deviations of other atoms from this plane are O(1)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34141 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

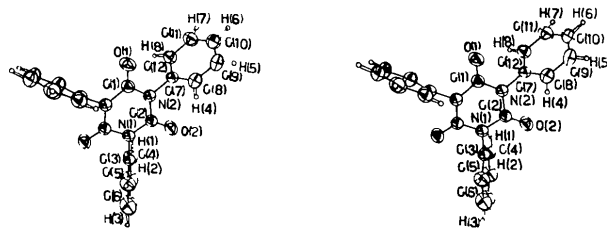


Fig. 1. The structure of phenylisocyanurate (the thermal ellipsoids are shown on a 50% probability scale).

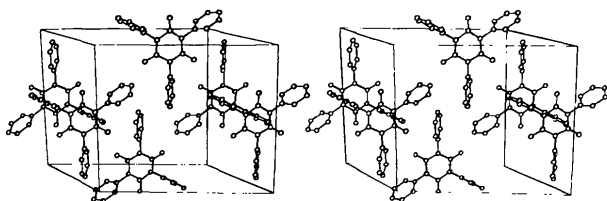


Fig. 2. Stereoscopic packing diagram of the molecules in the unit cell with H atoms omitted.

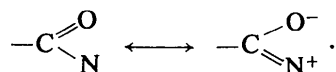
Table 2. Bond distances (Å) with *e.s.d.*'s in parentheses and bond angles (*e.s.d.*'s 0.1–0.2°)

		Corrected for riding motion*		
C(1)–O(1)	1.191 (3)	1.217	C(4)–H(1)	1.018 (25)
C(1)–N(2)	1.392 (2)	1.391	C(5)–H(2)	1.020 (27)
C(2)–N(2)	1.392 (2)	1.390	C(6)–H(3)	0.816 (41)
C(2)–N(1)	1.392 (2)	1.393	C(8)–H(4)	0.945 (24)
C(2)–O(2)	1.199 (2)	1.222	C(9)–H(5)	1.002 (29)
C(3)–N(1)	1.454 (3)	1.452	C(10)–H(6)	0.984 (30)
C(3)–C(4)	1.381 (2)	1.395	C(11)–H(7)	0.942 (30)
C(4)–C(5)	1.389 (3)	1.378	C(12)–H(8)	0.976 (24)
C(5)–C(6)	1.371 (3)	1.370		
C(7)–N(2)	1.453 (2)	1.454		
C(7)–C(8)	1.376 (2)	1.367		
C(7)–C(12)	1.377 (2)	1.382		
C(9)–C(10)	1.367 (3)	1.370		
C(10)–C(11)	1.375 (3)	1.372		
C(11)–C(12)	1.387 (3)	1.398		
O(1)–C(1)–N(2)	122.8		N(2)–C(7)–C(8)	119.6
N(2)–C(1)–N'(2)	114.4		N(2)–C(7)–C(12)	119.4
C(1)–N(2)–C(2)	125.1		C(8)–C(7)–C(12)	120.9
C(1)–N(2)–C(7)	116.6		C(7)–C(8)–C(9)	119.3
C(2)–N(2)–C(7)	118.3		C(7)–C(8)–H(4)	117.4
N(2)–C(2)–O(2)	122.4		C(9)–C(8)–H(4)	123.3
N(2)–C(2)–N(1)	114.9		C(8)–C(9)–C(10)	119.8
N(1)–C(2)–O(2)	122.7		C(8)–C(9)–H(5)	116.6
N(1)–C(3)–C(4)	119.3		C(10)–C(9)–H(5)	123.2
C(4)–C(3)–C'(4)	121.5		C(9)–C(10)–C(11)	120.8
C(3)–C(4)–H(1)	119.5		C(9)–C(10)–H(6)	118.7
C(3)–C(4)–C(5)	118.7		C(11)–C(10)–H(6)	120.4
C(5)–C(4)–H(1)	121.8		C(10)–C(11)–H(7)	117.0
C(4)–C(5)–C(6)	120.4		C(10)–C(11)–C(12)	119.9
C(4)–C(5)–H(2)	117.8		C(12)–C(11)–H(7)	123.1
C(6)–C(5)–H(2)	121.8		C(11)–C(12)–C(7)	119.3
C(5)–C(6)–C'(5)	120.5		C(11)–C(12)–H(8)	122.7
C(5)–C(6)–H(3)	119.8		C(7)–C(12)–H(8)	118.0
C(2)–N(1)–C'(2)	124.5		C(2)–N(1)–C(3)	117.7

* The correction factor is $(U_2 - U_1)/2R$, where U_2 and U_1 are the total mean-square displacements of atoms 2 and 1; R is the uncorrected bond length.

0.249, N(1) –0.031 and C(1) 0.165 Å. The benzene rings make angles of $72.9 \pm 0.2^\circ$ with the cyanuric ring.

Bond lengths and angles are listed in Table 2. The C–O length (1.191 Å) is shorter than usual (1.23 Å) and the C–N length (1.392 Å) longer than the C=N length (1.22 Å) which suggests that, in phenylisocyanurate, there is little resonance of the form



The shortness of the C–N length in the cyanuric ring compared with the standard single bond (1.47 Å) may be due to resonance with the phenyl groups. However, the C–N length (1.454 Å) connecting a phenyl group to the cyanuric ring is almost equal to a normal C–N single-bond length. Thus the type of resonance in the cyanuric ring seems to be a combination of both effects.

There is little evidence of strong hydrogen bonding. The shortest O...H distances are in the range 2.8–3.0 Å and the angles are wide. The molecules form a layer-like structure with the cyanuric rings parallel. Fig. 2 shows the packing in the unit cell.

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