

Crystal Structure of *N,N'*-bis-(β,β,β -trinitroethyl)urea

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Determination of the crystal structure of *N,N'*-bis(β,β,β -trinitroethyl)urea, $(\text{NO}_2)_3\text{CCH}_2\text{NHCONHCH}_2\text{C}(\text{NO}_2)_3$, has provided a detailed description, heretofore unavailable, of a crystallographically ordered structure in which there are three nitro groups bonded to the same carbon atom. The lengths of the C–N bonds joining the three nitro groups to the β -carbon atoms are, uncorrected for thermal motion, $1.51 \pm 0.015 \text{ \AA}$ (limits of error), which is significantly longer than the normal C–N single bond distance, 1.47 \AA . Also, the N–C–N bond angles around the β -carbon atoms are $2.3\text{--}4.7^\circ$ (limits of error = $\pm 0.8^\circ$) less than the tetrahedral value, and the corresponding N–C–C bond angles are $2.3\text{--}3.8^\circ$ ($\pm 0.8^\circ$) greater than the tetrahedral value. The structure of the central part of the molecule differs somewhat from that of the urea molecule. The crystals studied are orthorhombic with most probable space group *Pnn*2, $a = 10.47 \pm 0.02$, $b = 11.25 \pm 0.02$, $c = 5.85 \pm 0.01 \text{ \AA}$, and two molecules per unit cell. Each molecule is required by the space group to have a twofold axis. With 935 independent non-zero single-crystal diffractometer data, the structural parameters were refined by the method of least-squares to a conventional $R = 0.054$. Crystal data for the related compound $(\text{NO}_2)_3\text{CCH}_2\text{NHCONHCH}_2\text{NHCONHCH}_2\text{C}(\text{NO}_2)_3$ are also given.

Introduction

Wetterholm (1964) has discussed the synthesis and some of the physical and chemical properties of the compound *N,N'*-bis-(β,β,β -trinitroethyl)urea,



which, for convenience, will be designated BTNEU. He has shown that the synthesis yields a mixture of BTNEU and by-product compounds



(compound I) and



(compound II) in which $\text{R} \equiv \text{CH}_2\text{C}(\text{NO}_2)_3$. Single crystals of BTNEU and compound I have been isolated from the mixture by G. P. Espinosa of this laboratory, and the crystal structure of BTNEU has been determined. The primary reason for studying the compound was to determine the nature of the bonding of three nitro groups to a single carbon atom. The detailed geometry of a crystallographically ordered $-\text{C}(\text{NO}_2)_3$ structure has not been reported previously.

Experimental

M. B. Frankel of the Rocketdyne Division of North American Rockwell Corporation provided samples

Table 1. Crystallographic data

- (a) BTNEU
 Most probable space group: *Pnn*2– C_{2v}^{10}
 Lattice constants: $a = 10.47 \pm 0.02 \text{ \AA}$
 $b = 11.25 \pm 0.02$
 $c = 5.85 \pm 0.01$
 Unit-cell volume = 689 \AA^3
 Unit cell contains 2 $(\text{NO}_2)_3\text{CCH}_2\text{NHCONHCH}_2\text{C}(\text{NO}_2)_3$
 Formula weight = 386
 Calculated density = 1.86 g.cm^{-3}
 Measured density (flotation method) = $1.85 \pm 0.01 \text{ g.cm}^{-3}$
 Systematic absences: $0kl$ with $k+l$ odd; $h0l$ with $h+l$ odd
- (b) Compound I
 Most probable space group: *Cc*– C_s^4 or *C2/c*– C_{2h}^6
 Lattice constants: $a = 17.02 \pm 0.02 \text{ \AA}$
 $b = 11.36 \pm 0.02$
 $c = 9.27 \pm 0.02$
 $\beta = 91.8 \pm 0.1^\circ$
 Unit-cell volume = 1791 \AA^3
 Unit-cell contains 4 $(\text{NO}_2)_3\text{CCH}_2\text{NHCONHCH}_2\text{NHCONHCH}_2\text{C}(\text{NO}_2)_3$
 Formula weight = 458
 Calculated density = 1.70 g.cm^{-3}
 Measured density (flotation method) = $1.69 \pm 0.01 \text{ g.cm}^{-3}$
 Systematic absences: hkl with $h+k$ odd; $h0l$ with l odd

which were in the form of fine powders and which consisted of the mixture of compounds typically obtained in the BTNEU synthesis. Taking advantage of the substantially different solubilities of the compounds in methyl alcohol (Wetterholm, 1964), Espinosa isolated single crystals of BTNEU and single crystals which appear to be compound I by fractional recrystallization from this solvent. The procedure did not yield any crystals identifiable as compound II.

The most probable space groups and the lattice constants of the BTNEU and compound I crystals were determined from Mo $K\alpha$ Buerger precession photographs taken at 23°C. The crystallographic data are summarized in Table 1. In the case of BTNEU, the systematic absences are also characteristic of the space group $Pnmm-D_{2h}^{12}$, but this space group would require the BTNEU molecule to have $2/m$ symmetry, which is impossible.

Intensity data for the BTNEU crystals were measured with a Buerger-Supper-Pace-Picker automatic diffractometer, Mo $K\alpha$ radiation, and balanced Zr and Y filters. The crystal was rotated about the c axis. The continuous scan mode was used, with a scan rate of $\frac{1}{2}$ degree per minute, scan interval of 3° or more, and background counts of 3 minutes or more at the beginning and the end of the scan interval. All independent $I(hkl)$ with $(\sin \theta)/\lambda \leq 0.7$, a total of 1096, were measured. Of these, 942 were greater than the background intensity.

Because of deterioration of the crystals after prolonged exposure to X-rays, as shown by losses in the intensities of several reflections that were checked periodically during the measurements, it was necessary to use three different crystal specimens to obtain the intensity data. The first specimen was used to obtain reciprocal lattice level $l=0$ with no apparent decomposition, and was discarded later when the decomposition

first became detectable. The second specimen was used for levels $l=1-4$, and was discarded at the end of $l=4$, when the intensities of the check reflections had fallen to 90% of their original values. The third specimen was used for levels 5-8, during which there was no measurable decomposition because of the relatively short time required for these levels. Each crystal appeared to be stable for a few days and then began to deteriorate, slowly at first and later more rapidly. The crystals were originally transparent and colorless but became nearly opaque and yellow-brown in color after long exposure to X-rays.

The three crystals were essentially prismatic in shape with edge lengths 0.05-0.32 mm, 0.12-0.34 mm, and 0.07-0.56 mm, respectively. The intensities were corrected for absorption, although the corrections were small because of the small linear absorption coefficient of 2.0 cm⁻¹ for Mo $K\alpha$ radiation; the correction factors, computed by the method of Burnham (1966), were 1.01-1.05 for the first crystal, 1.03-1.04 for the second, and 1.03-1.05 for the third.

The intensities were reduced to relative $|F_o(hkl)|^2$ by application of the usual Lorentz-polarization and Tunell factors.

Determination of the structure and refinement of parameters

In space group $Pnn2$ the BTNEU molecule is required to have a twofold axis of symmetry with the central carbon and oxygen atoms on the symmetry axis. The central carbon and oxygen atoms, C(1) and O(1), were therefore arbitrarily taken to be in the $2(a)$ positions, 0, 0, z and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$, with $z=0$ for the carbon atom to define the origin. All other atoms are in the general positions, $4(c)$. The asymmetric unit of the structure consists of the central carbon and oxygen atoms and

Table 2. Positional and thermal parameters* and their estimated standard errors†

	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(1)	0	0	0	45 (4)	27 (2)	206 (12)	8 (2)	0	0
O(1)	0	0	2083 (10)	81 (4)	58 (3)	208 (10)	-13 (3)	0	0
N(1)	716 (3)	756 (2)	-1326 (9)	59 (2)	34 (2)	195 (7)	-11 (2)	4 (3)	-11 (3)
C(2)	1639 (3)	1544 (2)	-306 (10)	39 (2)	27 (2)	216 (8)	-1 (2)	-11 (3)	6 (3)
C(3)	1362 (3)	2828 (2)	-946 (9)	46 (2)	30 (2)	159 (8)	-5 (2)	-9 (3)	-3 (3)
N(2)	1702 (3)	3124 (3)	-3419 (9)	68 (3)	57 (2)	184 (8)	-9 (2)	-9 (4)	17 (3)
O(2)	2104 (4)	4108 (3)	-3808 (11)	179 (5)	76 (3)	270 (9)	-50 (3)	0 (6)	50 (5)
O(3)	1542 (3)	2325 (3)	-4772 (10)	129 (4)	82 (3)	193 (7)	-24 (2)	7 (4)	-19 (4)
N(3)	-24 (3)	3135 (2)	-618 (9)	56 (2)	39 (2)	279 (9)	3 (2)	0 (4)	-9 (3)
O(4)	-574 (3)	3618 (3)	-2191 (11)	85 (3)	80 (3)	380 (12)	26 (2)	-73 (5)	-12 (4)
O(5)	-473 (3)	2859 (3)	1222 (11)	90 (3)	87 (3)	383 (12)	18 (2)	87 (5)	23 (5)
N(4)	2129 (3)	3696 (2)	475 (10)	79 (3)	40 (2)	199 (8)	-15 (2)	-45 (4)	10 (3)
O(6)	1585 (3)	4570 (2)	1234 (10)	139 (4)	44 (2)	334 (10)	9 (2)	-72 (6)	-43 (4)
O(7)	3236 (3)	3438 (3)	706 (11)	78 (3)	81 (2)	395 (12)	-23 (2)	-72 (5)	-20 (4)
H(1)‡	1590	1452	1529						
H(2)‡	2575	1301	-863						
H(3)‡	660	698	-3026						

* The β_{ij} are for the expression $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$.

† The estimated standard errors $\times 10^4$ are given in parentheses.

‡ The values for the hydrogen atoms were assumed; the hydrogen atoms were given an isotropic thermal parameter $B=3.0 \text{ \AA}^2$ (see text for further discussion).

nitrogen, and oxygen. This was aided by an $hk0$ Patterson projection which indicated the approximate positions of the urea-like nitrogen atom N(1) and the other two carbon atoms, C(2) and C(3).

The parameters were refined by the method of least-squares, using the Busing, Martin & Levy (1962)

computer program *ORFLS*. In the least-squares calculations the function minimized was $\sum w(|F_o| - (1/k)|F_c|)^2$ in which k is a scale factor and w is a weighting function (for $|F_o| \geq 7.0$, $w = 200/|F_o|^2$; for $7.0 > |F_o| \geq |F_{o, \min}|$, $w = 4$). Only the $|F_o|$ above background were included in the least-squares calculations. Seven non-

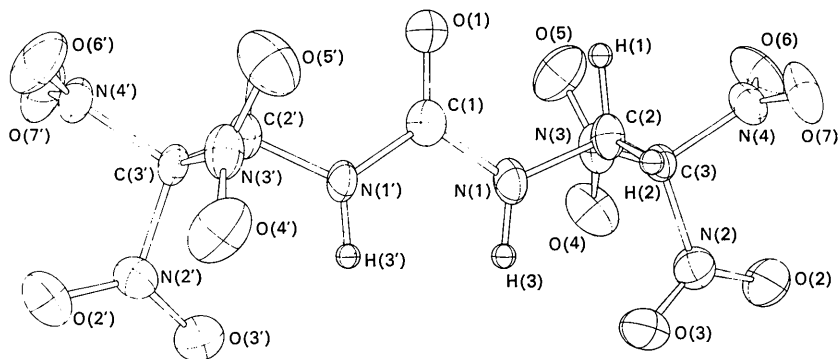


Fig. 1. Perspective drawing of the BTNEU molecule, viewed approximately along $[110]$; the hydrogen atoms H(1') and H(2') are hidden behind the atoms O(5') and N(3') respectively. Thermal motion probability ellipsoids correspond to 50% probability. The Figure was drawn with the Johnson (1965) computer program.

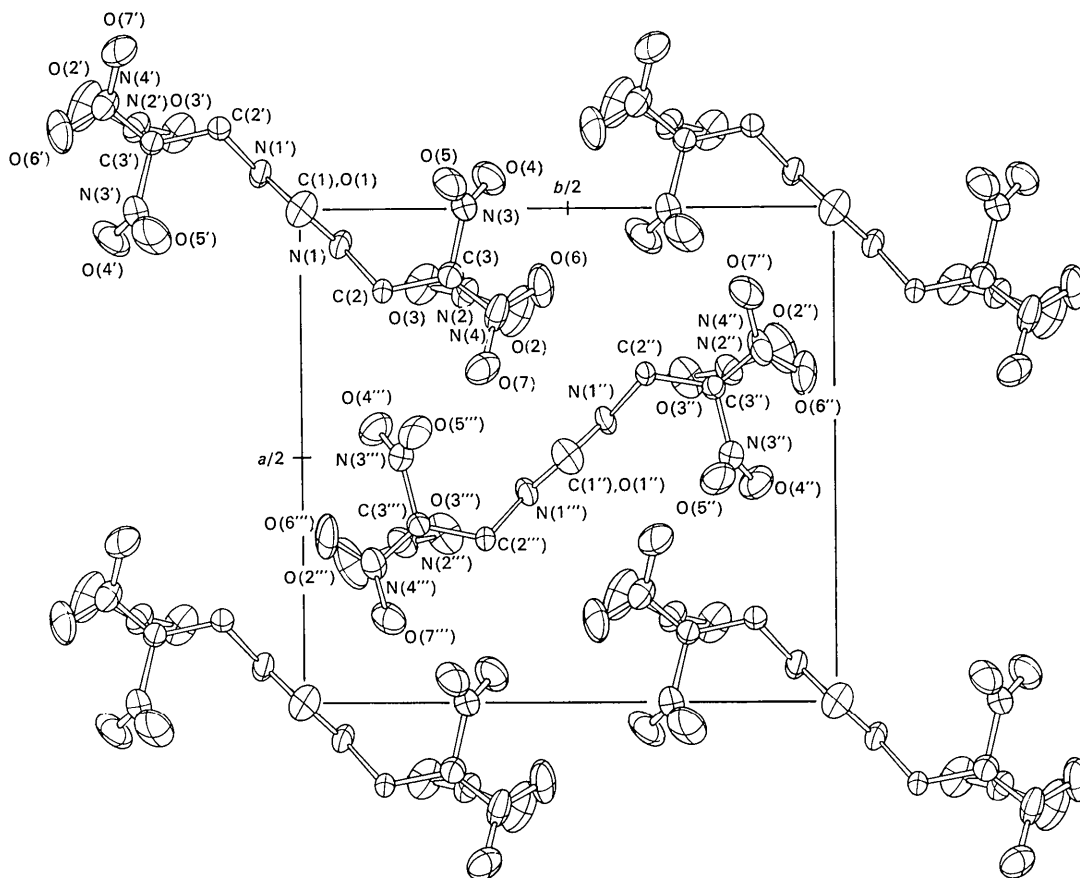


Fig. 2. Parallel projection of the structure on (001); the hydrogen atoms are not shown. Thermal motion probability ellipsoids correspond to 50% probability. The Figure was drawn with the Johnson (1965) computer program.

Table 4. Bond distances and angles*

(a) Bond distances			
C(1)–O(1)	1.22 ± 0.02 Å	N(2)–O(3)	1.21 ± 0.015 Å
C(1)–N(1)	1.37 ± 0.01	N(3)–O(4)	1.21 ± 0.015
N(1)–C(2)	1.44 ± 0.01	N(3)–O(5)	1.21 ± 0.015
C(2)–C(3)	1.52 ± 0.015	N(4)–O(6)	1.22 ± 0.015
C(3)–N(2)	1.53 ± 0.015	N(4)–O(7)	1.20 ± 0.015
C(3)–N(3)	1.50 ± 0.015		
C(3)–N(4)	1.51 ± 0.01		
N(2)–O(2)	1.21 ± 0.015		
(b) Bond angles			
O(1)–C(1)–N(1)	124.4 ± 0.6°	C(3)–N(3)–O(4)	117.7 ± 1.0°
N(1)–C(1)–N(1)	111.3 ± 1.2	C(3)–N(3)–O(5)	115.3 ± 0.9
C(1)–N(1)–C(2)	120.9 ± 0.9	O(4)–N(3)–O(5)	127.0 ± 1.0
N(1)–C(2)–C(3)	110.8 ± 0.8	C(3)–N(4)–O(6)	118.1 ± 0.9
C(2)–C(3)–N(2)	113.3 ± 0.7	C(3)–N(4)–O(7)	114.8 ± 0.9
C(2)–C(3)–N(3)	111.8 ± 0.7	O(6)–N(4)–O(7)	127.1 ± 0.9
C(2)–C(3)–N(4)	112.1 ± 0.8		
N(2)–C(3)–N(3)	107.2 ± 0.8		
N(2)–C(3)–N(4)	104.8 ± 0.7		
N(3)–C(3)–N(4)	107.1 ± 0.8		
C(3)–N(2)–O(2)	117.4 ± 0.9		
C(3)–N(2)–O(3)	115.2 ± 0.9		
O(2)–N(2)–O(3)	127.4 ± 1.1		

* The limits of error are $3 \times$ the estimated standard errors computed by the program *ORFFE*.

zero reflections were omitted from the least-squares calculations: the four $00l$ reflections, for which peak heights, rather than integrated intensities, were measured; 440 and 880, which are weak reflections on heavy streaks; and 101, which is one of the strongest reflections and is apparently strongly affected by extinction. However, during all refinement cycles, structure factors were calculated for the unobserved data and for all the omitted reflections. The scattering factors used were those given by Cromer & Waber (1965) for C, N, and O, and those for H from *International Tables for X-ray Crystallography* (1962).

In the first few refinement cycles the thermal parameters were kept isotropic and the hydrogen atoms were neglected. Subsequently the thermal parameters were allowed to become anisotropic. After several refinement cycles it appeared that inclusion of the hydrogen atoms in the calculation might remove some discrepancies between $|F_o|$ and $|F_c|$ which remained among the data with low values of $(\sin \theta)/\lambda$. Reasonable hydrogen positions were determined by making the N–H and C–H bond distances 1.00 and 1.07 Å, respectively, and by assuming a planar arrangement around the nitrogen atom, with the two C–N–H bond angles equal, and a tetrahedral arrangement around the carbon atom. The hydrogen atoms were given an isotropic temperature factor $B=3.0 \text{ \AA}^2$. With the hydrogen atoms included there was an immediate improvement in the agreement. With the hydrogen atom parameters held constant, the refinement was continued until the changes in the parameters were negligibly small compared with their estimated standard errors. The final parameter values are given in Table 2. The final value of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.054$. Table 3 compares

the $|F_o|$ with the $|F_c|$ calculated from the final parameter values.

Discussion of the structure

The structure is illustrated in Figs. 1 and 2. Bond distances, bond angles, and other interatomic distances of importance in the following discussion, computed with the Busing, Martin & Levy (1964) computer program *ORFFE*, are given in Tables 4, 5, and 6.

Table 5. Other intramolecular distances*

O(2)–O(3)	2.17 Å	O(3)–O(4)	3.05 Å
O(4)–O(5)	2.17	O(3)–O(5)	4.13
O(6)–O(7)	2.17	O(3)–O(6)	4.32
N(2)–N(3)	2.44	O(3)–O(7)	3.87
N(2)–N(4)	2.41	O(4)–O(6)	3.20
N(3)–N(4)	2.43	O(4)–O(7)	4.34
N(2)–O(4)	2.55	O(5)–O(6)	2.89
N(2)–O(5)	3.55	O(5)–O(7)	3.95
N(2)–O(6)	3.17	C(3)–O(2)	2.34
N(2)–O(7)	2.92	C(3)–O(3)	2.31
N(3)–O(2)	3.10	C(3)–O(4)	2.33
N(3)–O(3)	3.07	C(3)–O(5)	2.30
N(3)–O(6)	2.57	C(3)–O(6)	2.35
N(3)–O(7)	3.52	C(3)–O(7)	2.29
N(4)–O(2)	2.55	C(2)–N(2)	2.54
N(4)–O(3)	3.49	C(2)–N(3)	2.50
N(4)–O(4)	3.23	C(2)–N(4)	2.52
N(4)–O(5)	2.92	C(2)–O(3)	2.76
O(2)–O(4)	3.01	C(2)–O(5)	2.81
O(2)–O(5)	4.23	C(2)–O(7)	2.77
O(2)–O(6)	3.04	N(1)–O(3)	2.81
O(2)–O(7)	2.99	N(1)–N(3)	2.82

* The distances in this Table have limits of error ($=3 \times$ estimated standard errors) of $\pm 0.02 \text{ \AA}$.

Table 6. *Intermolecular distances**

Unprimed symbols refer to atoms at positions x, y, z in Table 1. Single prime, double prime, and triple prime refer, respectively, to atoms at positions $-x, -y, z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z; \text{ and } \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

O(4)–O(7''')	2.90 Å	O(2)–O(5''')	3.37 Å
O(2)–O(6)	2.99	O(2)–N(4)	3.37
O(4)–O(6')	3.05	O(3)–O(7)	3.42
O(5)–O(6')	3.12	N(1)–O(6'')	3.44
O(2)–O(4')	3.16	O(3)–O(6)	3.44
C(2)–O(2'')	3.17	C(2)–O(4''')	3.45
N(2)–O(5''')	3.17	O(6)–O(6')	3.46
O(3)–O(5''')	3.19	O(3)–H(1)	2.38
O(3)–O(5)	3.21	O(6)–H(2'')	2.73
O(1)–O(2'')	3.24	O(2)–H(2'')	2.77
O(3)–N(4)	3.24	O(5)–H(2''')	2.82
N(3)–O(6')	3.24	O(7)–H(3''')	2.82
N(1)–O(7''')	3.25	O(4)–H(2''')	2.89
C(1)–O(2'')	3.27	O(7)–H(3'')	2.89
N(1)–O(2'')	3.29	O(2)–H(1'')	2.98
O(5)–O(7''')	3.29	O(1)–H(3)	3.05
O(1)–O(7'')	3.31	O(4)–H(1''')	3.06
N(1)–O(7'')	3.32	O(6)–H(3'')	3.18
N(3)–O(7''')	3.33	N(4)–H(3'')	3.35
O(4)–O(4')	3.34	H(1)–H(3)	3.44
C(2)–O(3)	3.35		

* The distances in this Table, except those involving hydrogen atoms, have limits of error ($= 3 \times$ estimated standard errors) of ± 0.02 Å.

An objective of this investigation was to determine the departure from normal bond distances and angles required for the bonding of three nitro groups to the same carbon atom. The lengths of the three crystallographically independent C–N bonds joining the three nitro groups to the β -carbon atoms, C(3), are, uncorrected for thermal motion, 1.51 ± 0.015 Å. Correction for thermal motion by the method of Busing, Martin & Levy (1964), with the reasonable assumption that the nitrogen atoms ride on the carbon atom, increases these bond distances by 0.01 Å. Thus the C–N bond distances are significantly longer than the normal C–N single bond distance, 1.47 Å. Also, the N–C–N and N–C–C bond angles around the β -carbon atoms are significantly different from the tetrahedral value: the three independent N–C–N angles are all less than the tetrahedral value by $2.3 \pm 0.8^\circ$ to $4.7 \pm 0.8^\circ$, while the corresponding N–C–C angles are all greater than the tetrahedral value by $2.3 \pm 0.8^\circ$ to $3.8 \pm 0.8^\circ$.

The three crystallographically independent nitro groups are identical in structure within the accuracy of the present results and their geometry is very similar to that reported previously for nitro groups by many others. The N–O bond distances, uncorrected for thermal motion, are 1.21 ± 0.015 Å. Correction for thermal motion, with the assumption that the oxygen atoms ride on the nitrogen atoms, increases these distances by 0.02 to 0.03 Å. The O–N–O bond angles are $127.2 \pm 1.1^\circ$, the O–N–C bond angles are $116.4 \pm 1.0^\circ$, and the non-bonded distance between the two oxygen atoms of

each nitro group is 2.17 ± 0.02 Å. The sums of the three bond angles around each of the three nitrogen atoms are 360° , which shows that in each nitro group the N–O and N–C bonds are coplanar.

Bonding of three nitro groups to the same carbon atom results in three intramolecular N–O distances of 2.56 ± 0.02 Å, which is substantially less than the sum of the van der Waals radii, 2.9 Å; these involve all three nitrogen atoms and one oxygen atom from each nitro group. However, the other N–O distances and the O–O distances are equal to or greater than the sums of the van der Waals radii.

The structure of the central part of the BTNEU molecule differs somewhat from that of the urea molecule. In BTNEU, the N–C–O and N–C–N bond angles at the central carbon atom are $124.4 \pm 0.6^\circ$ and $111.3 \pm 1.2^\circ$ respectively. These values differ significantly from the values of Caron & Donohue (1964) for the corresponding angles in urea, 120.5° and 119.0° . In BTNEU, the C–O and C–N bond distances of the central carbon atom, C(1), uncorrected for thermal motion, are 1.22 ± 0.02 and 1.37 ± 0.01 Å respectively. Correction of the C–O bond distance for thermal motion, with the assumption that the oxygen atom rides on the carbon atom, increases this distance by 0.02 Å. Correction of the C–N bond distance, also with the riding assumption, makes only a negligible change in this distance. These bond distances may be compared with the corrected values of 1.28 and 1.36 Å reported by Caron & Donohue (1964) for the urea molecule. The difference in the C–O bond distance is possibly significant but, within experimental error, the C–N bond distances are the same. For each compound the crystal symmetry requires that the C–O and C–N bonds be coplanar, with the sum of the bond angles equal to 360° , and that the two N–C–O angles be equal. The N(1)–C(2) bond distance is 1.44 ± 0.01 Å which is substantially greater than the C(1)–N(1) bond distance but still significantly shorter than the normal single bond value. The C(2)–C(3) bond distance, 1.52 ± 0.015 Å, is slightly less than the normal C–C single-bond value. Corrections of the N(1)–C(2) and C(2)–C(3) bond distances for thermal motion, with the riding assumption, are negligibly small.

The intramolecular distance N(1)–O(3) of 2.81 ± 0.015 Å is about 0.1 Å shorter than the sum of the van der Waals radii. This may indicate a weak hydrogen bond between these atoms through the hydrogen atom attached to N(1). This interaction, though weak, may be important in stabilizing the structure and inhibiting rotations or large amplitude oscillations of the nitro groups.

Table 6 gives all independent intermolecular contacts less than 3.5 Å. All these distances are greater than the sums of the van der Waals radii of the atoms involved.

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The Crystal Structure of the Anthracene–Tetracyanoethylene Adduct and Complex, $8C_{20}H_{10}N_4 \cdot 2CH_2Cl_2 \cdot C_6N_4$

BY ISABELLA L. KARLE AND A. V. FRATINI*†

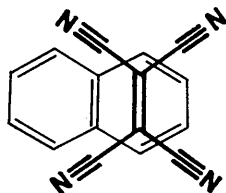
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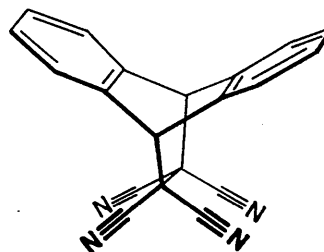
A complex consisting of eight anthracene–tetracyanoethylene adducts, two methylene chloride molecules and one free tetracyanoethylene molecule crystallizes in a triclinic cell, space group $P\bar{1}$, with cell dimensions $a = 13.40$, $b = 17.01$, $c = 20.36$ Å (all ± 0.03 Å), $\alpha = 99.8$, $\beta = 94.2$ and $\gamma = 129.1^\circ$ (all $\pm 0.3^\circ$). The 104 atoms in the asymmetric unit were located using the symbolic addition procedure for phase determination. Short intermolecular approaches, as low as 3.16 Å, exist between the C atom of one $C\equiv N$ group and the N atom of a $C\equiv N$ group from another molecule. In addition, intermolecular approaches as short as 3.4 Å exist between the free tetracyanoethylene molecule and the methylene chloride molecules.

Introduction

The crystal structure of the 1:1 molecular complex naphthalene–tetracyanoethylene (TCNE) which has been reported recently (Williams & Wallwork, 1967) shows that the two planar molecules are oriented in such a way as to facilitate a Diels–Alder reaction,



However, this reaction does not proceed under the conditions of crystallization. By contrast, such a reaction has been observed at room temperature between anthracene and TCNE to form an adduct, 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile,



(Middleton, Heckert, Little & Krespan, 1958). Greenish-yellow crystals of an anthracene–TCNE adduct were grown from a CH_2Cl_2 solution by Dr Craig Eckardt* at Yale University. The cell parameters of the triclinic cell, along with the measured density, indicated nine molecules of adduct in the unit cell, or $4\frac{1}{2}$ molecules per asymmetric unit if the space group were $P\bar{1}$ as indicated by the statistical distribution of intensities. Since the anthracene–TCNE adduct molecule does not have a center of symmetry, it was possible that the space group was $P1$, that a partial disorder existed, or that a free TCNE and a free anthracene molecule were present at some of the centers of symmetry. As the structure analysis progressed, it became apparent that these suppositions were not correct, but that the con-

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