planar arrangement, as, in principle, free rotation around the C(1)—P bond is possible. It seems very likely, that not only interaction with the neighboring *tert*-butyl group and a maximum degree of intermolecular hydrogen bonding, but also the possibility of acquiring additional stabilization by the intramolecular H···O contact contribute to the final geometry.

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[Methylenebis(*N*,*N'*-dimethylurea)]hydrogen(I) Trifluoromethanesulfonate,* C₇H₁₇N₄O₂⁺·CF₃O₃S⁻: a Very Strong Intramolecular O···H···O Bond

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Abstract. $M_r = 338.3$, triclinic, $P\bar{1}$, $a = 7.055$ (1), $b = 9.582$ (1), $c = 11.955$ (8) Å, $\alpha = 83.92$ (4), $\beta = 82.14$ (3), $\gamma = 70.36$ (1)°, $V = 752.5$ Å³, $Z = 2$, $D_x = 1.493$ g cm⁻³, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 2.62$ cm⁻¹, $F(000) = 352$, $T = 297$ K, $R = 0.0528$ for 2160 observed reflections. A very short hydrogen bond connects the two carbonyl oxygen atoms of the diurea, so that an eight-membered ring is formed, O···O 2.420 (3) Å. The anion is associated with two cations by hydrogen bonds of the N—H···O type: N···O 2.908 (3) and 2.855 (3) Å.

Introduction. Several examples of *inter*molecularly proton-connected assemblies of two carbonyl units are known and their structures have been determined, *e.g.* for urea (Zhang, Shao, Xu & Tang, 1981), acetamide (Groth, 1977; Muir & Speakman, 1979) or benzo-homotropone (Childs, Faggiani, Lock & Varadarajan, 1984). These systems belong to the HX_2^+ type (where X is a heteroatom). In contrast, most *intra*molecular hydrogen bonds between two carbonyl oxygen atoms, whose geometries have been investigated so far, belong to the HX_2^- type (Emsley, 1980; Olovsson & Jönsson, 1976). Apart from protonated bis(1,2-dihydro-1,5-dimethyl-3-oxo-2-phenyl-3*H*-pyrazol-4-yl)methane (Burschka, Akgun & Pindur, 1983), the title compound is the only example of an intramolecular hydrogen bond of the HX_2^+ type connecting two carbonyl groups. The structure of the former compound was, however, not completely refined, and no hydrogen atoms were localized. The intramolecular hydrogen bond, in that case, was indicated by an O···O contact of 2.47 (1) Å.

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* (4,6-Dimethyl-2,4,6,8-tetraaza-3,7-nonanedione)hydrogen(I) trifluoromethanesulfonate.

Experimental. The preparation of the title compound has been described elsewhere (Maas, Brückmann & Feith, 1985). Crystals were obtained by slow evaporation of an acetonitrile solution in a desiccator. A crystal of size $0.7 \times 0.4 \times 0.1$ mm was coated with Nujol and enclosed in a quartz capillary. Enraf–Nonius CAD-4 diffractometer, monochromatized Mo $K\alpha$ radiation. Cell parameters obtained from least-squares refinement of diffractometer settings for 24 reflections with $20.00 < 2\theta < 25.68°$. Data collection: θ from 2.0 to $25.0°$, θ–2θ scan, $h\,\bar{8}{\to}0$, $k\,\bar{11}{\to}10$, $l\,\bar{14}{\to}14$, 2655 independent reflections, scan width $(0.95 + 0.35\tan\theta)°$, scan speed 1.8 to $5.0°$ min^{-1}. 495 reflections with $I < 2\sigma(I)$ considered unobserved. Three monitor reflections showed an average intensity loss of 0.9%, accounted for by linear correction. Empirical absorption correction applied (ψ scans, transmissions 0.97 to 0.99). Structure solution by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), hydrogen atoms located in a difference Fourier map. Refinement by a full-matrix least-squares method, based on F, non-hydrogen atoms with anisotropic, hydrogen atoms with isotropic temperature factors, $w = [\sigma^2(F_o) + 0.00009F_o^2]^{-1}$, 258 variables, $R = 0.0528$, $wR = 0.0451$, $\Delta_{max}/\sigma < 0.65$, maximum residual electron density 0.22 e Å^{-3}. Programs of Enraf–Nonius (1983) *SDP* used throughout. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final positional and equivalent isotropic thermal parameters are given in Table 1, bond distances and angles in Table 2.* Fig. 1 shows the molecular structure of the cation.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen positions and bond geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42157 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
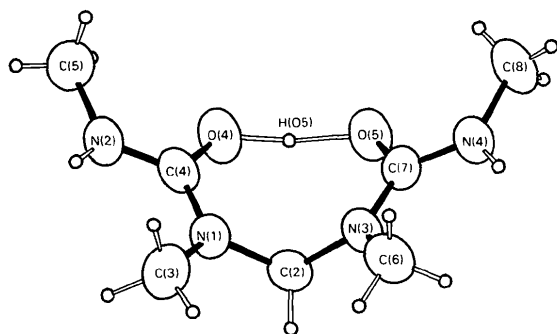
The cation is symmetrical with respect to bond distances and angles involving corresponding atoms: All differences are less than 1.95σ $[\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}]$. The torsion angles around N(1)—C(4) and N(3)—C(7), respectively, are significantly different, however: C(2)—N(1)—C(4)—O(4) $-3.4\,(4)°$ vs C(2)—N(3)—C(7)—O(5) $-10.8\,(4)°$, and C(3)—N(1)—C(4)—N(2) $175.3\,(4)°$ vs C(6)—N(3)—C(7)—N(4) $169.3\,(4)°$.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
S	0.2332 (1)	0.26271 (8)	0.25546 (6)	3.84 (2)
F(1)	0.1541 (4)	0.4647 (2)	0.3983 (2)	9.88 (7)
F(2)	0.0082 (4)	0.5375 (3)	0.2493 (3)	13.1 (1)
F(3)	0.3172 (4)	0.5070 (2)	0.2441 (2)	11.73 (8)
O(1)	0.0641 (3)	0.2245 (2)	0.3113 (2)	5.65 (5)
O(2)	0.4187 (3)	0.1917 (2)	0.3018 (2)	6.21 (6)
O(3)	0.2478 (3)	0.2695 (3)	0.1348 (2)	6.80 (6)
O(4)	−0.2434 (2)	0.1795 (2)	0.9012 (2)	4.67 (5)
O(5)	−0.2784 (2)	0.1583 (2)	0.7057 (2)	4.33 (5)
N(1)	0.1010 (3)	0.1097 (2)	0.8659 (2)	3.72 (5)
N(2)	−0.0747 (3)	0.2565 (3)	1.0128 (2)	4.46 (6)
N(3)	0.0646 (3)	0.1002 (2)	0.6664 (2)	3.64 (5)
N(4)	−0.1512 (3)	0.2076 (2)	0.5298 (2)	4.15 (6)
C(1)	0.1728 (5)	0.4527 (4)	0.2875 (3)	6.6 (1)
C(2)	0.0992 (4)	0.0197 (3)	0.7759 (2)	3.87 (7)
C(3)	0.2933 (4)	0.1220 (4)	0.8884 (3)	5.72 (8)
C(4)	−0.0747 (4)	0.1825 (3)	0.9258 (2)	3.74 (6)
C(5)	−0.2593 (5)	0.3490 (4)	1.0728 (3)	6.03 (9)
C(6)	0.2372 (4)	0.1186 (4)	0.5928 (3)	5.12 (8)
C(7)	−0.1240 (4)	0.1550 (3)	0.6355 (2)	3.56 (6)
C(8)	−0.3497 (4)	0.2857 (4)	0.4940 (3)	5.68 (9)

Table 2. *Bond distances* (Å) *and bond angles* (°)

Values for corresponding distances and bonds in the cation are arranged in parallel columns.

Cation

C(2)—N(1)	1.453 (4)	C(2)—N(3)	1.455 (3)
N(1)—C(3)	1.462 (4)	N(3)—C(6)	1.451 (4)
N(1)—C(4)	1.348 (3)	N(3)—C(7)	1.344 (3)
C(4)—O(4)	1.275 (3)	C(7)—O(5)	1.275 (3)
C(4)—N(2)	1.319 (4)	C(7)—N(4)	1.323 (3)
N(2)—C(5)	1.449 (3)	N(4)—C(8)	1.448 (3)
O(4)—H(O5)	1.12 (4)	O(5)—H(O5)	1.32 (4)

		N(1)—C(2)—N(3)	114.7 (3)
C(2)—N(1)—C(3)	119.3 (2)	C(2)—N(3)—C(6)	118.5 (2)
C(2)—N(1)—C(4)	119.5 (2)	C(2)—N(3)—C(7)	119.9 (2)
C(3)—N(1)—C(4)	121.2 (2)	C(6)—N(3)—C(7)	121.6 (2)
N(1)—C(4)—O(4)	121.1 (3)	N(3)—C(7)—O(5)	121.6 (2)
N(1)—C(4)—N(2)	120.3 (3)	N(3)—C(7)—N(4)	119.6 (2)
O(4)—C(4)—N(2)	118.6 (2)	O(5)—C(7)—N(4)	118.9 (2)
C(4)—N(2)—C(5)	122.6 (3)	C(7)—N(4)—C(8)	122.6 (2)

Anion

S—O(1)	1.424 (2)	F(1)—C(1)	1.326 (4)
S—O(2)	1.415 (2)	F(2)—C(1)	1.284 (4)
S—O(3)	1.428 (2)	F(3)—C(1)	1.316 (5)
S—C(1)	1.796 (4)		

O(1)—S—O(2)	115.6 (1)	S—C(1)—F(1)	110.9 (2)
O(1)—S—O(3)	114.5 (1)	S—C(1)—F(2)	112.5 (3)
O(1)—S—C(1)	102.8 (2)	S—C(1)—F(3)	102.5 (2)
O(2)—S—O(3)	114.7 (1)	F(1)—C(1)—F(2)	108.2 (3)
O(2)—S—C(1)	103.0 (2)	F(1)—C(1)—F(3)	106.2 (3)
O(3)—S—C(1)	103.8 (2)	F(2)—C(1)—F(3)	107.2 (3)

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the cationic part. The size of the thermal ellipsoids represents a 50% probability. One hydrogen atom at C(2) is hidden.

The salient feature of the cation is the very strong intramolecular hydrogen bond O(4)···H(O5)···O(5) connecting the two carbonyl groups, so that an eight-membered ring structure is generated. The short O(4)···O(5) distance [2·420 (3) Å] could suggest a centered hydrogen bond (Olovsson & Jönsson, 1976; Vinogradov & Linnell, 1971). However, the least-squares-refined position of H(O5) [$B = 12$ (1) Å^2], corresponds to a slightly asymmetrical situation. It is well known that asymmetry of an O···H···O bond in a seemingly symmetrical molecule can be induced even by small geometric differences beyond the neighboring heavy-atom bonds. In the present case, the above-mentioned differences in torsion angles (the shorter O···H contact is directed to the more planar half of the cation) and the force field of a neighboring anion [the intermolecular hydrogen bond involving H(N2) is shorter by 0·05 Å than the one involving H(N4)] may constitute such geometric differences. Definite description of the bond situation has to await more reliable determination of the hydrogen position either by a low-temperature X-ray analysis or by neutron diffraction and analysis of the hydrogen's thermal motion. Similar strong intramolecular hydrogen bonds as in the title compound have been reported for dicarboxylates, [H(RCO$_2$)$_2$]$^-$ (Emsley, 1980). Intermolecular bonds of the HX$_2^+$ type, realized in proton-connected dimers of carbonyl units like urea, acetamide or a benzo-homotropone (for references, see *Introduction*), O···O values of 2·44 to 2·45 Å, are apparently not much longer. In all cases, the strong O···H···O bond leads to considerable lengthening of the C=O bond. This is also true for the title compound, where the C—O distances [1·275 (2) Å] are markedly longer and the C—NHMe distances [1·321 (3) Å] shorter than in neutral methyl-urea with 1·248 (1) Å for C—O, 1·336 (2) Å for C—NHMe (Huiszoon & Tiemessen, 1976). The C—O values are close to those found in the bis(acetamide) hydrochloride [1·265 (1) Å] (Muir & Speakman, 1979) or hydrobromide complexes [1·264 (4) Å] (Groth, 1977) as well as to the C—O distance in O-protonated
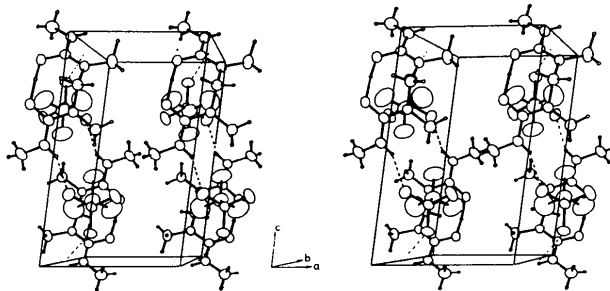
Table 3. Dimensions of the N—H···O hydrogen bonds between cation and anion

N(2)···O(3)	2·908 (3) Å	N(4)···O(1)	2·855 (3) Å
N(2)—H(N2)	0·80 (2)	N(4)—H(N4)	0·84 (2)
H(N2)···O(3)	2·14 (2)	H(N4)···O(1)	2·11 (2)
N(2)—H(N2)···O(3)	161 (2)°	N(4)—H(N4)···O(1)	148 (2)°

Symmetry code: $x, y, z + 1$ for O(3); x, y, z for all others.

N-methylurea [1·28 (2) Å] (Bryden, 1957). The changes of C—O and C—N bond lengths in ureas by hydrogen bonding have been discussed (Blessing, 1983). Classical carboxamide resonance structures can be used to explain the observed changes. It should be noted that the pseudocyclic C—N bonds [C(7)—N(3), C(4)—N(1)] are longer than the 'exocyclic' ones, contrary to the expectations for the higher degree of N-alkylation (Blessing, 1983). Stabilization of the corresponding carboxamide resonance structure by the intermolecular N—H···O hydrogen bonds gives a reasonable explanation.

A stereoscopic view of the unit cell is given in Fig. 2. The hydrogen atoms at N(2) and N(4) are each involved in a hydrogen bond to an oxygen atom of a trifluoromethanesulfonate anion. In this manner, one anion connects two cations, thereby building up infinite chains (cation–anion–cation . . .) along the c axis. The dimensions of these N—H···O bonds are sampled in Table 3. A recent survey shows that N···O values of 2·8–2·9 Å are encountered most frequently in inter-molecular hydrogen bonds and that the angle at hydrogen is grouped around 161° (Taylor, Kennard & Versichel, 1984).

Fig. 2. Stereoscopic view of the unit cell. Projection is along **b**.*

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$C_7H_{17}N_4O_2^+.CF_3O_3S^-$

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Tetrabenzotricyclo[5.5.0.0²,⁸]dodeca-3,5,9,11-tetraene,* C₂₈H₂₀

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Abstract. $M_r = 356.47$, orthorhombic, *Pbca*, $a = 12.765$ (4), $b = 12.905$ (3), $c = 22.139$ (7) Å, $V = 3647$ (3) Å³, $Z = 8$, $D_x = 1.30$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 0.068$ mm⁻¹, $F(000) = 1504$, $T = 295$ K, $R = 0.042$ for 2821 observed reflections. The central four-membered ring is puckered [30.3 (1)°]. The transannular C···C distances are 2.155 (2) Å. The seven-membered rings are strained with bond angles of 124.1 (1) and 125.7 (2)°. The biphenyl groups are twisted. The molecule shows only small deviations from 4̄ symmetry.

Introduction. Intramolecular thermal and photochemical [2+2]cycloadditions in 5-*trans*-15-*trans*-tetrabenzo-[*a,c,g,i*]cyclododecene (2) and its *cis–cis*- and *cis–trans*-isomers result in 1,2- and 1,3-substituted cyclobutane derivatives (Wittig & Skipka, 1975). The crystal structures of these olefins have been determined (Irngartinger, 1972, 1973*a,b*; Roberts & Kennard, 1973). Conformation *A* has been found in the crystal of (2). Photochemical intramolecular cycloaddition of (2) results in 1,2-substituted cyclobutane but thermal reaction by melting (2) at 583 K leads to a 1,3-substituted one, tetrabenzotricyclo[5.5.0.0²,⁸]dodeca-3,5,9,11-tetraene (1) (Wittig & Skipka, 1975). This reaction starts probably from conformation *B* of (2). We now describe the crystal structure of (1) which is strained. Because of electronic 'through-bond' interactions *via* the cyclobutane ring (Gleiter, Haider, Spanget-Larsen & Bischof, 1983; Spanget-Larsen, Gleiter & Haider, 1983), the crystal structure of (1) is of additional interest.

(1)

A   B

(2)

(3)

(4)
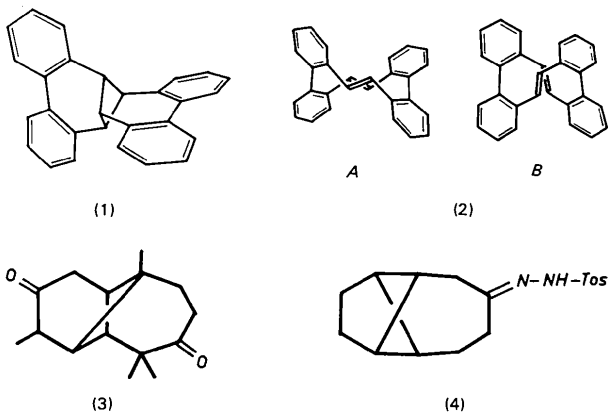
Experimental. Crystal 0.4 × 0.4 × 0.3 mm, grown from ethyl acetate; CAD-4 diffractometer (Enraf–Nonius), cell dimensions from 2θ angles of 25 reflections ($16 < 2\theta < 33°$); 4387 data up to $2\theta = 56°$ (excluding systematic absences), $0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 29$, standard reflections $\overline{3}42$, $\overline{4}3\overline{2}$ and 624 (variation of intensities less than 3%), 4387 unique reflections; Lorentz and polarization corrections applied; absorption and extinction effects neglected; 2821 intensities, $I > 3\sigma(I)$; structure solution by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); structure refined by full-matrix least squares on F^2 with anisotropic thermal parameters for C atoms. Positions of H atoms calculated according to geometrical requirements. H atoms refined isotropically. 333 variables, $R = 0.042$, $wR = 0.047$ for 2821 reflections, $w = 4F^2/\sigma^2(F^2) + (0.03F^2)^2$; $S = 1.89$; $\Delta/\sigma < 0.05$, largest peak = 0.18 e Å⁻³; scattering factors from *International Tables for X-ray Crystallography* (1974);