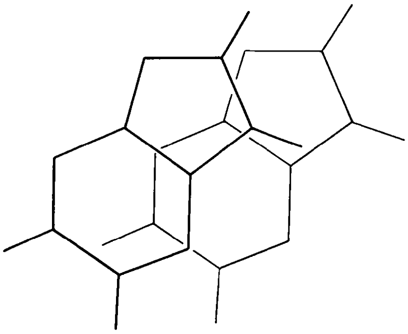

Fig. 3. Stacking of the molecules.

differences involve C(3)—N(4), which is considerably longer than in 5-(*p*-chlorophenyl)-1,2,4-triazine and imidazole. Simple LCAO calculations for imidazole, 1,2,4-triazine and the title compound with the parameters suggested by Streitwieser (1961) have been carried out and the resulting π-bond orders are listed in Table 2. There is a reasonable correlation between the bond lengths and the bond orders (Fig. 2); in particular, the relatively long C(3)—N(4) in the title compound is reflected in a low bond order.

The molecules are planar within the limits of accuracy and are stacked in tightly packed columns along [001], the distance between the planes of adjacent molecules being 3·36 Å. The stacking is indicated in Fig. 3. The packing of the columns is depicted in Fig. 4 in a projection of the structure along [001]. All contacts between the columns correspond to normal van der Waals distances.

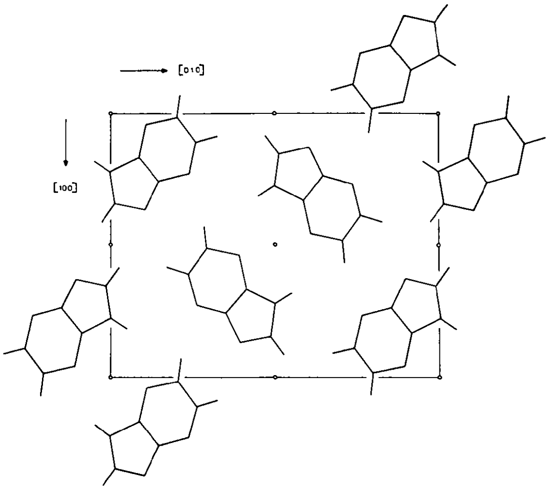

Fig. 4. Projection of the structure along [001].

Our thanks are due to Mr D. Heijdenrijk for technical assistance.

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An Antitumor Agent, 2-(3,3-Dimethyl-1-triazeno)phenyl-1-carboxamide*

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Abstract. $C_9H_{12}ON_4$, monoclinic, $P2_1/c$, $a = 9{\cdot}444(5)$, $b = 7{\cdot}085(4)$, $c = 16{\cdot}005(7)$ Å, $\beta = 108{\cdot}08(4)°$, $Z = 4$, $D_x = 1{\cdot}257(1)$, $D_m = 1{\cdot}25(1)$ g cm^{-3}, at 23 °C. Its structure is similar to that of $C_6H_{11}ON_6$, a related antitumor agent reported earlier; both have an internal hydrogen bond.

Introduction. The sample was provided by Dr Corwin Hansch of Pomona College. Two distinct crystalline forms grew from the pure sample dissolved in toluene. The predominant form, which was orthorhombic, appeared to include a molecule of toluene in the asymmetric unit (according to its density, cell volume and mass-spectroscopy information). Investigation of the other (monoclinic) form suggested that it did not include the solvent molecule, and it was used for the structure determination.

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Photographic X-ray diffraction data revealed systematic absences, $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$, indicating the space group $P2_1/c$. A single crystal, 0·07 × 0·08 × 0·21 mm in size, was mounted on a full-circle Picker Nuclear FACS-I automated diffractometer. Data were collected in the hemisphere with k non-negative and $\sin\theta/\lambda < 0{\cdot}54$, with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}70926$ Å for α_1) and the θ–2θ scan technique. The data were averaged to give 1339 independent reflections, of which 108 were recorded as zero. The absorption parameter (μ) is 0·53 cm^{-1}, which was considered small enough to be ignored. The intensity decay of three regularly monitored reflections was less than 2% during the experiment, and no correction was made for this effect.

The crystal structure was solved by interpretation of the Patterson function and the use of *MULTAN* (Germain, Main & Woolfson, 1971), with essentially the same result.

After preliminary refinement of the heavy atoms, eleven of the H atoms were found on a difference Fourier map. The position of the remaining H atom was calculated. Tentative refinement of the H parameters was unsatisfactory. The two amide H atoms were then constrained to the positions found in the Fourier maps, while the others were held at positions calculated for C—H = 0·97 Å. The methyl hydrogens were constrained to tetrahedral geometry, rotated for greatest overlap with the electron density map. An overall isotropic temperature parameter for all H atoms was refined to a value of $B = 9{\cdot}4$ (7) Å^2. For the non-H atoms, the positional and anisotropic thermal parameters were refined. When refinement was concluded, no parameter shift was more than 3% of the corresponding standard deviation. Weights were derived from $\sigma^2(F^2) = s^2 + (pF^2)^2$, where s^2 is the variance according to counting statistics and $p = 0{\cdot}05$ was chosen to equalize $\langle w(\Delta F)^2\rangle$ for strong and weak reflections. The final residual $R_w\{= [\Sigma\, w(\Delta F)^2/\Sigma\, wF_o^2]^{1/2}\}$ was 0·053 for 563 reflections with $F^2 > 2\sigma$. The unweighted residual $R(=\Sigma|\Delta F|/\Sigma|F_o|)$ was 0·059 for the same data. For all data, R was 0·166. The refinement was calculated by our full-matrix least-squares program with the atomic scattering factors of Doyle & Turner (1968), and the anomalous scattering corrections of Cromer & Liberman (1970) for neutral C, N and O, and those of Stewart, Davidson & Simpson (1965) for spherical H. Final parameters are given in Tables 1 and 2.*

Table 1. *Positional parameters*

	x	y	z
C(1)	0·2514 (8)	0·350 (1)	0·2876 (5)
C(2)	0·1001 (9)	0·349 (1)	0·2478 (5)
C(3)	0·0414 (8)	0·376 (1)	0·1569 (6)
C(4)	0·1356 (9)	0·397 (1)	0·1081 (5)
C(5)	0·2897 (7)	0·400 (1)	0·1467 (4)
C(6)	0·3475 (7)	0·380 (1)	0·2376 (4)
N(7)	0·5054 (5)	0·3871 (8)	0·2778 (3)
N(8)	0·5403 (6)	0·4115 (9)	0·3611 (4)
N(9)	0·6843 (6)	0·4146 (8)	0·4003 (3)
C(10)	0·7939 (7)	0·392 (1)	0·3550 (5)
C(11)	0·7303 (7)	0·450 (1)	0·4946 (4)
C(12)	0·3771 (8)	0·432 (1)	0·0839 (5)
O(13)	0·3100 (5)	0·4624 (8)	0·0052 (3)
N(14)	0·5255 (7)	0·4269 (8)	0·1135 (3)
H(1)	0·295	0·334	0·351
H(2)	0·031	0·333	0·281
H(3)	−0·066	0·379	0·129
H(4)	0·090	0·407	0·045
H(5)	0·803	0·510	0·327
H(6)	0·761	0·293	0·311
H(7)	0·888	0·358	0·397
H(8)	0·643	0·458	0·514
H(9)	0·785	0·567	0·507
H(10)	0·793	0·347	0·525
H(11)	0·556	0·424	0·179
H(12)	0·578	0·418	0·078

Table 2. *Anisotropic thermal parameters* (Å^2)

The temperature-factor expression is
$\exp[-(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \cdots)/4]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3·8 (4)	7·3 (5)	5·4 (4)	0·2 (4)	1·5 (4)	−1·9 (4)
C(2)	4·5 (4)	9·2 (6)	7·3 (5)	0·4 (4)	2·5 (4)	−3·2 (5)
C(3)	3·8 (4)	6·9 (5)	8·2 (5)	0·4 (4)	0·5 (4)	−2·6 (5)
C(4)	5·0 (4)	3·5 (4)	6·1 (4)	0·6 (4)	0·3 (3)	−1·0 (4)
C(5)	3·8 (4)	4·4 (4)	4·5 (3)	−0·4 (3)	0·7 (3)	0·1 (4)
C(6)	3·6 (3)	4·5 (4)	4·4 (4)	1·0 (3)	0·7 (3)	−1·0 (4)
N(7)	4·4 (3)	3·9 (3)	3·5 (3)	0·2 (3)	1·2 (2)	0·4 (3)
N(8)	4·1 (3)	4·7 (3)	3·9 (3)	−0·3 (3)	0·8 (2)	0·6 (3)
N(9)	4·0 (3)	5·7 (4)	3·8 (3)	0·1 (3)	0·3 (2)	0·2 (3)
C(10)	4·0 (3)	5·7 (5)	6·0 (4)	0·1 (3)	1·6 (3)	−0·0 (4)
C(11)	6·3 (4)	7·8 (6)	3·8 (3)	0·1 (4)	−0·1 (3)	0·9 (4)
C(12)	5·6 (4)	4·2 (4)	4·0 (4)	−0·6 (4)	0·3 (3)	0·5 (4)
O(13)	6·9 (3)	9·4 (4)	3·9 (2)	−2·0 (3)	0·0 (2)	1·7 (3)
N(14)	5·5 (3)	7·7 (4)	3·9 (3)	−0·2 (3)	1·7 (2)	−0·4 (3)

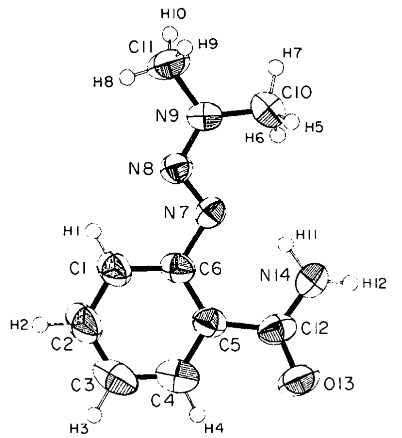

Fig. 1. Molecular structure and numbering scheme for the DTPC molecule.

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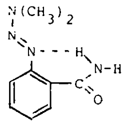
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32102 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

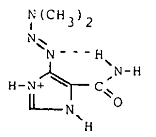
Table 3. *Bond lengths of DTPC and corresponding values for DTIC* (Å)

	DTPC	DTIC
C(1)–C(2)	1·37 (1)	
C(2)–C(3)	1·40 (1)	
C(3)–C(4)	1·36 (1)	
C(4)–C(5)	1·39 (1)	
C(5)–C(6)	1·39 (1)	
C(6)–C(1)	1·40 (1)	
C(6)–N(7)	1·429 (8)	1·378 (3)
N(7)–N(8)	1·281 (7)	1·288 (3)
N(8)–N(9)	1·309 (7)	1·305 (3)
N(9)–C(10)	1·45 (1)	1·446 (3)
N(9)–C(11)	1·46 (1)	1·449 (3)
C(5)–C(12)	1·50 (1)	1·463 (3)
C(12)–O(13)	1·24 (1)	1·226 (3)
C(12)–N(14)	1·33 (1)	1·328 (3)
N(14)–H(11)	1·00	
N(14)–H(12)	0·87	

Discussion. This study was undertaken to determine the structural similarity between 2-(3,3-dimethyl-1-triazeno)phenyl-1-carboxamide (DTPC) and 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide (DTIC, Edwards, Sherfinski & Marsh, 1974). Both of these compounds belong to a class of related antitumor agents currently being studied for potency and effectiveness.



DTPC



DTIC cation

The DTPC molecule (Fig. 1) is approximately planar, due in part to bond conjugation through the phenyl ring and triazene group. The carboxamide group is held coplanar by the internal hydrogen bond N–H···N, with N–N = 2·71 (1) Å.

There is great similarity between DTPC and DTIC, which can be seen from a comparison of bond lengths given in Table 3. An important similarity between the two structures is the internal hydrogen bond. In DTIC, the N–N distance of this hydrogen bond is 2·97 Å, while in DTPC the more favorable bond angles in the phenyl ring allow N–N = 2·71 Å. The existence of this internal hydrogen bond lends credence to the mechanism of deactivation of bis(chloroethyl)triazenoimidazolecarboxamide proposed earlier by Edwards, Sherfinski & Marsh (1974). The internal hydrogen bond may be important in explaining the success of similar antitumor agents.

Table 4. *Bond angles* (°)

C(6)–C(1)–C(2)	120·1 (7)	N(7)–N(8)–N(9)	113·3 (5)
C(1)–C(2)–C(3)	120·1 (7)	N(8)–N(9)–C(10)	123·8 (5)
C(2)–C(3)–C(4)	119·5 (7)	N(8)–N(9)–C(11)	115·6 (5)
C(3)–C(4)–C(5)	121·7 (7)	C(10)–N(9)–C(11)	120·6 (5)
C(4)–C(5)–C(6)	118·6 (6)	C(4)–C(5)–C(12)	114·9 (6)
C(5)–C(6)–C(1)	119·9 (6)	C(6)–C(5)–C(12)	126·5 (6)
C(5)–C(6)–N(7)	118·9 (6)	C(5)–C(12)–O(13)	119·4 (6)
C(1)–C(6)–N(7)	121·3 (6)	C(5)–C(12)–N(14)	119·6 (6)
C(6)–N(7)–N(8)	111·7 (5)	O(13)–C(12)–N(14)	121·0 (6)

The second amide H atom, H(12), provides a hydrogen bond to the O atom of a neighboring molecule, with N(14)–O(13) = 2·91 (1) Å.

Bond angles are in Table 4.

We thank Dr Corwin Hansch for providing the sample.

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