The mean C—C bond distances in the other four six-membered rings are 1·375 (10) [C(10) to C(15)], 1·377 (11) [C(17) to C(22)], 1·379 (21) [C(23) to C(28)], and 1·378 (8) Å [C(29) to C(34)], where the e.s.d.'s are based on the variations of the lengths. The corresponding mean values for the C—C—C bond angles are 120·0 (1·0), 120·0 (1·8), 120·0 (1·6), and 120·0 (1·3)°. The least-squares-planes' calculations show the phenyl rings to be essentially planar, and they are all approximately perpendicular to the cyclohexane least-squares plane forming angles of 80·0, 91·6, 85·8, and 110·7°.

The H atom H(O4) can be regarded as providing a hydrogen bond within the molecule with $O(4)\cdots O(3)$ 2·831 (4), O(4)—H(O4) 0·87 (3), $H(O4)\cdots O(3)$ 2·16 (4) Å, O(4)—H(O4)···O(3) 133 (4)°, and simultaneously another somewhat weaker interaction with $O(1^i)$ of an adjacent molecule, $O(4)\cdots O(1^i)$ 2·970 (4), $H(O4)\cdots O(1^i)$ 2·29 (3) Å, $O(4)—H(O4)\cdots O(1^i)$ 134 (3)°. The angle $O(3)\cdots H(O4)\cdots O(1^i)$ is 90 (1)°, and thus H(O4) lies in the plane through the three O atoms O(4), O(3), and $O(1^i)$. The intramolecular hydrogen bond is therefore somewhat weakened due to the attractive force exerted by the next O(1) atom of the molecule related by the symmetry operation $1-x$, $1-y$, $-z$. For the molecule in solution, however, one can expect that the intramolecular hydrogen bond gains importance.

The packing of the molecules viewed along $\mathbf{b_0}$ is depicted in Fig. 2.

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A Reinvestigation of the Structure of Bis(2-fluoro-2,2-dinitroethyl)nitramine, C4H4F2N6O10

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Abstract. $M_r = 334·1$, monoclinic, $P2_1$, $a = 5·972$ (1), $b = 18·180$ (4), $c = 10·669$ (3) Å, $\beta = 92·25$ (1)°, $V = 1157·5$ (8) Å^3, $D_x = 1·917$ Mg m^{-3}, $Z = 4$, $\lambda(Cu\,K\alpha) = 1·5418$ Å, $\mu = 1·904$ mm^{-1}, $T = 294$ K, $F(000) = 672$. Final $R = 0·027$ for 1916 observed reflections. The two crystallographically independent molecules have distinct conformations and symmetries (C_2 and C_s). A previous crystal structure report [Atovmyan, Gafurov, Golovina & Eremenko (1978). *Sov. Phys. Dokl.* **23**, 539–540] indicated that the conformer with the shorter intramolecular contacts was involved with the longer intermolecular contacts and *vice versa*, in support of the authors' hypothesis that 'van der Waals bonds possess the property of saturability'. The present investigation was carried out to examine further this interesting hypothesis. On the basis of a 0·4 Å^3 difference in the calculated molecular volumes and a comparison of the inter- and intramolecular contacts, it is concluded that there are no significant differences in the molecular environments of the two molecules.

Introduction. We are investigating the crystal structures of a number of high-density, $CF(NO_2)_2$-containing compounds, which are of interest as possible organic explosives. Our crystallographic work on the title compound (I)

$$[FC(NO_2)_2—CH_2]_2N—NO_2$$

(I)
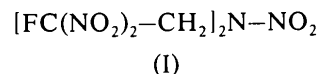
was in the preliminary stages at the time of a structure report by Atovmyan, Gafurov, Golovina & Eremenko (1978) (AGGE). The crystal structure contains two molecules per asymmetric unit, but is somewhat unusual in that the molecules adopt different conformations. On the basis of a comparison of a number of intra- and intermolecular distances, AGGE proposed that 'the van der Waals bonds possess the property of saturability'. That is, the molecule with the shorter, non-bonded intramolecular contacts would be associated with the longer intermolecular contacts, and *vice versa*. Their report did not contain a list of atomic coordinates that could be used to examine further this most intriguing idea and, therefore, we have redetermined the crystal structure. We find that there are no significant differences in the overall intra- and intermolecular environments of the conformers.

Experimental. Obtained from Dr H. Adolph, Naval Surface Weapons Center, White Oak, Maryland, as transparent needles, $0.49 \times 0.25 \times 0.25$ mm; cell parameters determined and intensity measurements made with a Picker FACS-I diffractometer, graphite-monochromated Cu radiation; unit-cell parameters determined by least squares from 2θ values of 11 reflections manually centered at $\pm 2\theta$ (average $|2\theta_o - 2\theta_c| = 0.007°$); intensities measured by the θ–2θ scan technique, scan rate $2°$ min^{-1}, 20 s backgrounds, 2θ scan width calculated from $1.8° + 0.3°$ tan θ, four standards monitored at 100-reflection intervals, maximum intensity variation of standard reflections $<1\%$; total of 1946 reflections measured to $2\theta_{max} = 126°$, maximum $h,k,l = 6,21,12$, and minimum $h,k,l = 0,0,-12$; 1935 unique, 1916 3σ above background; structure could not be solved with the *MULTAN*80 programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), solution readily obtained with a set of programs (negative quartets utilized) being developed for the new *XTAL* system (Hall, Stewart & Munn, 1980); E map with 415 data revealed positions of all C, N, O and F atoms; structure refined by block-diagonal least squares with anisotropic temperature factors for the C, N, O and F atoms and isotropic terms for the H atoms; quantity minimized $\sum w(F_o - F_c)^2$, $w = [1/\sigma(F)]^2$, reflections for which $I_c < 3\sigma(I)$ not included in refinement; maximum least-squares shift/error ratio 0.919; no absorption or secondary-extinction corrections; maximum and minimum height in final difference map ± 0.16 e Å^{-3}; scattering factors for C, N, O and F atoms calculated from analytical expressions of Cromer & Mann (1968), H terms interpolated from the tabulated values of Stewart, Davidson & Simpson (1965), final R and R_w 0.027 and 0.029 respectively; majority of the calculations performed on a Univac 1108 computer at the University of Maryland's Computer Science Center with the XRAY system (Stewart, Machin, Dickinson,

Ammon, Heck & Flack, 1976) of crystallographic programs.

Discussion. Atomic coordinates and thermal parameters are listed in Table 1.*

ORTEP drawings (Johnson, 1971) of the two molecules in the asymmetric unit are shown in Fig. 1. The most interesting aspect of this crystal structure is the finding that the two crystallographically unique molecules have totally different conformations, and yet each conformer possesses a high degree of internal

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38714 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and temperature factors (Å^2) with e.s.d.'s in parentheses*

	x	y	z	U_{eq} or U
(a) C_s molecule				
C(1)	0.5017 (6)	0	0.9560 (3)	0.037 (2)†
C(2)	0.4871 (5)	−0.0684 (2)	1.0375 (3)	0.032 (6)†
C(1')	0.5653 (5)	−0.2016 (2)	0.8001 (3)	0.038 (7)†
C(2')	0.5238 (5)	−0.1964 (2)	0.9394 (2)	0.034 (7)†
N(1)	0.3933 (4)	−0.1310 (1)	0.9683 (2)	0.029 (6)†
N(2)	0.1638 (4)	−0.1425 (2)	0.9784 (2)	0.041 (6)†
N(3)	0.2698 (6)	0.0261 (2)	0.9077 (3)	0.037 (3)†
N(4)	0.6001 (5)	0.0655 (2)	1.0269 (3)	0.040 (5)†
N(3')	0.3467 (5)	−0.2102 (2)	0.7209 (2)	0.048 (8)†
N(4')	0.7012 (4)	−0.2695 (2)	0.7695 (3)	0.043 (8)†
O(2)	0.0574 (4)	−0.0926 (1)	1.0235 (2)	0.063 (7)†
O(3a)	0.2144 (7)	0.0085 (2)	0.8026 (3)	0.060 (4)†
O(3b)	0.1632 (5)	0.0594 (2)	0.9823 (3)	0.071 (5)†
O(4a)	0.6421 (5)	0.1189 (1)	0.9632 (3)	0.067 (5)†
O(4b)	0.6244 (6)	0.0594 (2)	1.1390 (3)	0.041 (6)†
O(2')	0.0890 (4)	−0.2008 (1)	0.9387 (2)	0.039 (7)†
O(3a')	0.2629 (5)	−0.1538 (2)	0.6826 (3)	0.094 (8)†
O(3b')	0.2777 (5)	−0.2725 (2)	0.7084 (3)	0.037 (8)†
O(4a')	0.7638 (5)	−0.2723 (2)	0.6615 (3)	0.099 (9)†
O(4b')	0.7367 (5)	−0.3136 (1)	0.8502 (3)	0.079 (9)†
F(1)	0.6278 (4)	−0.0109 (1)	0.8575 (2)	0.085 (2)†
F(1')	0.6727 (4)	−0.1439 (1)	0.7577 (2)	0.063 (7)†
H(2a)	0.634 (5)	−0.082 (2)	1.071 (3)	0.041 (9)
H(2b)	0.399 (5)	−0.058 (2)	1.107 (3)	0.027 (8)
H(2a')	0.671 (5)	−0.193 (2)	0.983 (3)	0.036 (9)
H(2b')	0.447 (5)	−0.243 (2)	0.967 (3)	0.041 (9)
(b) C_2 molecule				
C(1)	−0.0764 (5)	0.2214 (2)	0.6613 (3)	0.032 (9)†
C(2)	−0.1072 (5)	0.1386 (2)	0.6602 (3)	0.03 (1)†
C(1')	−0.0511 (5)	0.0067 (2)	0.4488 (3)	0.03 (1)†
C(2')	−0.1108 (5)	0.0874 (2)	0.4373 (3)	0.03 (1)†
N(1)	−0.2245 (4)	0.1136 (2)	0.5462 (2)	0.03 (1)†
N(2)	−0.4536 (4)	0.1090 (2)	0.5453 (3)	0.04 (1)†
N(3)	−0.2962 (4)	0.2629 (1)	0.6812 (2)	0.038 (9)†
N(4)	0.0819 (4)	0.2456 (2)	0.7700 (2)	0.03 (1)†
N(3')	−0.2578 (5)	−0.0433 (2)	0.4390 (3)	0.05 (1)†
N(4')	0.0946 (5)	−0.0182 (2)	0.3419 (3)	0.03 (1)†
O(2)	−0.5441 (4)	0.1321 (2)	0.6382 (3)	0.06 (1)†
O(3a)	−0.4029 (4)	0.2812 (2)	0.5885 (2)	0.064 (9)†
O(3b)	−0.3462 (4)	0.2702 (2)	0.7894 (2)	0.07 (1)†
O(4a)	0.1364 (4)	0.3096 (1)	0.7707 (3)	0.04 (1)†
O(4b)	0.1402 (5)	0.1994 (1)	0.8446 (2)	0.05 (1)†
O(2')	−0.5472 (4)	0.0830 (2)	0.4515 (2)	0.04 (1)†
O(3a')	−0.3344 (6)	−0.0614 (2)	0.5355 (3)	0.11 (1)†
O(3b')	−0.3292 (4)	−0.0563 (2)	0.3327 (3)	0.04 (1)†
O(4a')	0.1782 (5)	−0.0787 (2)	0.3555 (3)	0.07 (1)†
O(4b')	0.1119 (5)	0.0234 (2)	0.2555 (3)	0.08 (1)†
F(1)	0.0065 (3)	0.2469 (1)	0.5563 (2)	0.053 (9)†
F(1')	0.0589 (4)	−0.0089 (1)	0.5556 (2)	0.05 (1)†
H(2a)	−0.193 (6)	0.124 (2)	0.738 (3)	0.06 (1)
H(2b)	−0.031 (5)	0.116 (2)	0.667 (3)	0.033 (8)
H(2a')	−0.217 (6)	0.099 (2)	0.357 (3)	0.05 (1)
H(2b')	0.021 (5)	0.119 (2)	0.426 (3)	0.042 (9)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

symmetry. The molecular symmetries are very nearly C_2 (the dyad is coincident with the N—N bond) and C_s (the mirror is normal to the N—NO$_2$ plane and coincident with the N—N bond). The extents to which the molecules satisfy these symmetry descriptions were investigated by comparing the appropriate sets of O—N—N—C—CF(NO$_2$)$_2$ coordinates with Nyburg's (1974) best-molecular-fit program. R.m.s. deviations of 0·043 and 0·063 Å, respectively, were obtained for the C_2 and C_s molecules. While these values indicate that the symmetries are not exact, the correspondence is remarkable in view of the many small C—N and C—C rotations that could occur, resulting in substantially larger deviations but not in appreciable violations of the overall symmetry.

The conformations of the C—CF(NO$_2$)$_2$ groups between C_2 and C_s molecules are similar, with best-molecular-fit r.m.s. deviations that range from 0·020 to 0·066 Å. There are no apparently bad contacts in either of the nitramines and the principal differences appear to be due to differences in the N—CH$_2$ dihedral angles which orient the CH$_2$—CF(NO$_2$)$_2$ arms about the central N—NO$_2$ core.

A complete list of bond lengths and angles is given in Table 2. Several of our distances differ substantially from those in the earlier report (AGGE) (bond angles were not included in their paper). Bond lengths and angles are for the most part very similar in the two molecules. There is, however, an interesting pattern of differences between the two N—NO$_2$ groups. For example, the sum of the angles around the nitramine N atoms at 354·2 (5) and 359·8 (5)° in the C_s and C_2 molecules suggests a subtle difference in nitrogen hybridization. This difference is reflected in the associated N—N distances, which are 1·395 (3) and 1·370 (3) Å. There is also a slight difference in the N—O distances. Taken together, these differences indicate that mesomeric structure (IIb) makes a larger contribution to the nitramine resonance hybrid in the C_2 molecule than in the C_s molecule.

(IIa) ⟷ (IIb)
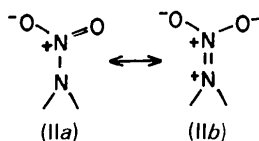
The volumes of the two molecules were calculated (Holden, 1982) by summing the appropriate atomic volumes (Kitaigorodsky, 1973) and correcting for atom–atom overlap where necessary. The values of 216·4 and 216·8 Å^3 obtained for the C_2 and C_s molecules are essentially identical, reflecting the similar intramolecular environments in these species. The corresponding volumes reported by AGGE of 209·7 (C_2) and 202·9 (C_s) Å^3 differ from our findings not so much in terms of magnitude but in the 6·8 Å^3 difference between the C_2 and C_s volumes.
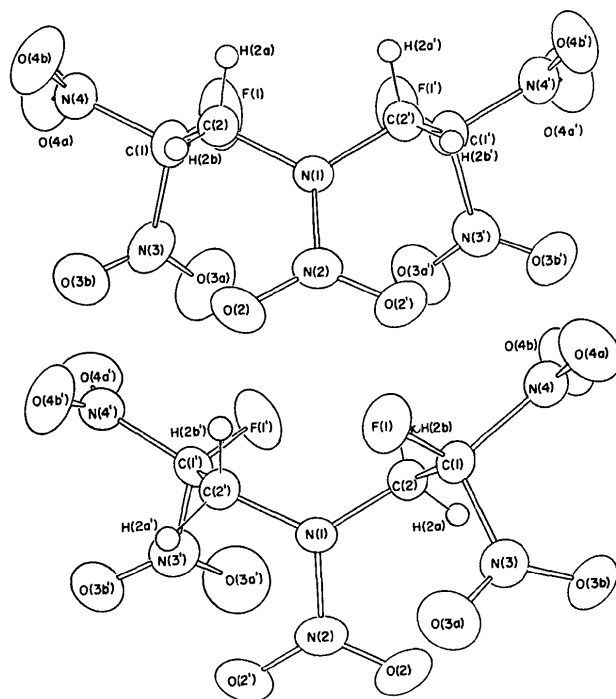

Fig. 1. *ORTEP* drawings of the C_s (top) and C_2 (bottom) molecules with the C, N, O and F atoms depicted as 50% probability boundary ellipses. H atoms are shown as 0·1 Å radius circles.

Table 2. *Bond lengths (Å) and angles (°) of the C_s and C_2 molecules with e.s.d.'s in parentheses*

The two sets of columns under the symmetry symbols refer to lengths and angles that are related by the molecular symmetries. Values in the right-hand columns of each set are obtained from the primed coordinates in Table 1.

	C_s		C_2	
C(1)–F(1)	1·332(4)	1·318(4)	1·327(3)	1·324(4)
C(1)–C(2)	1·521(4)	1·519(4)	1·517(5)	1·513(4)
C(1)–N(3)	1·534(5)	1·535(4)	1·536(4)	1·534(4)
C(1)–N(4)	1·516(3)	1·520(4)	1·531(4)	1·529(4)
N(1)–N(2)	1·395(3)	—	1·370(3)	—
N(1)–C(2)	1·457(4)	1·461(4)	1·453(4)	1·449(4)
N(2)–O(2)	1·217(4)	1·219(4)	1·221(4)	1·223(4)
N(3)–O(3a)	1·200(4)	1·204(5)	1·202(4)	1·189(5)
N(3)–O(3b)	1·203(4)	1·211(4)	1·211(4)	1·219(4)
N(4)–O(4a)	1·218(4)	1·226(4)	1·208(4)	1·215(4)
N(4)–O(4b)	1·205(4)	1·189(4)	1·199(4)	1·200(4)
F(1)–C(1)–C(2)	112·1(2)	112·7(2)	112·9(2)	112·7(3)
F(1)–C(1)–N(3)	108·1(2)	107·9(2)	107·1(2)	107·5(3)
F(1)–C(1)–N(4)	106·9(2)	107·6(2)	107·4(2)	107·5(2)
C(2)–C(1)–N(3)	111·9(2)	112·1(2)	112·6(2)	112·5(2)
C(2)–C(1)–N(4)	112·7(2)	111·7(2)	111·2(2)	111·5(2)
N(3)–C(1)–N(4)	104·6(2)	104·4(2)	105·1(2)	104·7(2)
C(2)–N(1)–C(2')	123·0(2)	—	123·3(2)	—
C(2)–N(1)–N(2)	115·9(2)	115·3(2)	118·2(2)	118·3(2)
C(1)–C(2)–N(1)	112·2(2)	111·5(2)	111·8(2)	111·7(2)
N(1)–N(2)–O(2)	116·6(3)	116·8(2)	116·6(3)	116·9(3)
O(2)–N(2)–O(2')	126·5(3)	—	126·5(3)	—
C(1)–N(3)–O(3a)	116·4(3)	115·7(3)	116·8(3)	116·2(3)
C(1)–N(3)–O(3b)	115·3(3)	115·7(3)	115·4(2)	115·4(3)
O(3a)–N(3)–O(3b)	128·3(4)	128·5(3)	127·7(3)	128·3(3)
C(1)–N(4)–O(4a)	115·6(3)	114·8(3)	116·1(3)	115·0(3)
C(1)–N(4)–O(4b)	116·9(3)	118·3(3)	117·1(3)	117·1(3)
O(4a)–N(4)–O(4b)	127·5(3)	126·9(3)	126·8(3)	127·9(3)

Table 3. *Average intra- and intermolecular non-bonded distances* (Å)

The quantity following each slash is the number of distances averaged for the contact.

	C_s	C_2
Intramolecular		
F	2·780/20	2·846/20
O(C–NO₂)	2·909/64	2·890/60
O(N–NO₂)	2·834/16	2·845/16
Intermolecular		
F	3·493/10	3·364/13
O(C–NO₂)	3·391/65	3·338/71
O(N–NO₂)	3·433/20	3·402/20

On the basis of previous work, AGGE had proposed that the more 'a molecule is stressed, the more loosely it is packed in the crystal'.* In support of this hypothesis (see *Introduction*), they tabulated the average intra- and intermolecular contacts for the F and O atoms in the two conformers, which showed that the conformer (C_s) with the longer intramolecular contacts is the same one that is associated with the shorter intermolecular contacts. Unfortunately, the precise boundary conditions used in these tabulations were not reported and we have been unable to repeat their calculations exactly with our atomic-coordinate data. Our calculations were carried out in the following manner: the intra- and intermolecular contacts were limited to those less than 3·8 Å, and no more than 10 of the shortest contacts to a particular atom were used to construct the appropriate non-bonded contact averages. These data, which are summarized in Table 3, show no significant trends that could be interpreted as support for the AGGE hypothesis. We find, in fact, that it is the C_s conformer, not the C_2 conformer, which is involved in the shorter intramolecular/longer intermolecular contacts. The

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* This quotation is from a translation of the original Russian paper. We believe that the word 'strain' would be more in line with common chemical usage than 'stress'. The inference here is to intramolecular, non-bonded contacts.

tabulated data further show that it is primarily the F···F contacts that provide a basis for concluding that the C_s conformer is associated with the shorter intramolecular contacts.

These data, in conjunction with our calculated molecular volumes, indicate that there are no significant differences between the intra- and intermolecular environments of the two molecules. While the hypothesis of AGGE in the matter of the saturability of van der Waals contacts may be valid, it is our conclusion that the crystal structure in question cannot be used to support this idea.

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3'-Fluorobiphenyl-4-carboxylic Acid, C₁₃H₉FO₂

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Abstract. $M_r = 216·2$, monoclinic, $P2_1/c$, $a = 3·92$ (1), $b = 8·04$ (1), $c = 32·50$ (2) Å, $\beta = 101·6$ (1)°, $V = 1003·4$ Å³, $Z = 4$, $D_m = 1·42$, $D_x = 1·43$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 0·927$ mm⁻¹, $F(000) = 448$, $T = 293$ K, $R = 0·087$ for 899 observed reflexions. The structure was solved by Patterson synthesis from densitometer and visually measured equi-inclination Weissenberg data. The average C—C bond in the phenyl ring is 1·389 Å. The molecule is non-planar; the angle between the phenyl rings is 36·3 (0·6)° and the

0108-2701/83/111568-03$01.50