Asp158–Lys137 and His81–Glu52) and a charge network involving Glu35, Arg17, Glu50 and Arg83. In addition the following buried charge groups are adequately compensated for by non-charge group interactions or are partially solvent accessible; Asp55, Glu52, Glu57, Glu135, Lys178 and Lys215. The rings of Trp181, Tyr86 and Tyr207 have unusual χ_2 values, judged by comparison with those observed by Ponder & Richards (1987), owing to steric hindrance of the rings. Lys64 has an unusual conformation (χ_1) determined by its contacts with the symmetry-related molecule and Thr42 also has a somewhat unusual χ_1 owing to hydrogen bonding. Finally, it is interesting to note that ppΩ is a less-flexible molecule than papain (Fig. 4) despite a similar number of crystal contacts and this observation may be related to its higher stability than that of papain.

Program *PACK* was written by Dr J. Warwicker and the authors acknowledge his help in using this program.

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Studies on 1,3-Diaryltriazene Analogues of Berenil: Molecules with Potential GC Base-Pair Selectivity

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Abstract

1,3-Bis(4-acetylphenyl)triazene (II): $C_{16}H_{15}N_3O_2$, $M_r = 281\cdot32$, monoclinic, $P2_1/c$, $a = 14\cdot002$ (5), $b = 12\cdot359$ (3), $c = 8\cdot457$ (3) Å, $\beta = 96\cdot35$ (2)°, $V = 1454\cdot5$ Å^3, $Z = 4$, $D_x = 1\cdot287$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54178$ Å, $\mu = 0\cdot672$ mm^{-1}, $F(000) = 592$, $T = 294$ K, final $R = 0\cdot089$ for 1890 unique observed reflections. 1,3-Bis{4-[2-(dimethylamino)ethoxycarbonyl]phenyl}triazene monohydrate (III): $C_{22}H_{29}$-$N_5O_4.H_2O$, $M_r = 445\cdot52$, triclinic, $P\bar{1}$, $a = 9\cdot500$ (2), $b = 11\cdot753$ (3), $c = 13\cdot328$ (2) Å, $\alpha = 62\cdot84$ (1), $\beta = 66\cdot60$ (2), $\gamma = 77\cdot58$ (2)°, $V = 1214\cdot1$ Å^3, $Z = 2$, $D_x = 1\cdot172$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54178$ Å, $\mu = 0\cdot640$ mm^{-1}, $F(000) = 476$, $T = 294$ K, final $R = 0\cdot063$ for 1100 unique observed reflections. Both crystal structures have extended conformations for the 1,3-diaryltriazene groups, with a *cisoid* arrangement of phenyl rings. The terminal N—N bonds of each triazene are non-equivalent, and a hydrogen atom has been located in the N=N—NH moiety. Extensive molecular-orbital (MNDO) calculations on the model core 1,3-diphenyltriazene system have confirmed that this geometry is energetically favoured, and have revealed the shape of the energy surface for rotation about the N—NH bond in the triazene linkage.

Introduction

The recognition of specific nucleotide sequences in DNA by small molecules has recently been the subject of considerable study. Drugs such as netropsin

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and distamycin have concave shapes (Berman, Neidle, Zimmer & Thrum, 1979; Goodsell & Dickerson, 1986) that complement the minor groove surface of AT regions of DNA, as shown by crystal structure analyses of netropsin– and distamycin–olignonucleotide complexes (Kopka, Yoon, Goodsell, Pjura & Dickerson, 1985*a*; Coll, Frederick, Wang & Rich, 1987; Coll, Aymami van der Marel, van Boom, Rich & Wang, 1989). It is generally accepted that the AT selectivity of these and other DNA ligands is due to a combination of steric, electrostatic and hydrogen-bonding factors (Pullman & Pullman, 1981; Kopka, Yoon, Goodsell, Pjura & Dickerson, 1985*b*). Alterations of the AT recognition shown by netropsin have been attempted with some success, with the synthesis of analogues having hydrogen-bond donor/acceptor features capable, in principle, of interacting with GC base pairs (Lown, 1988).

The anti-trypanosomal agent berenil (I) [1,3-bis(4-amidinophenyl)triazene; 'diminazene'] similarly binds to AT-rich DNA (Newton, 1975; Braithwaite & Baguley, 1980; Baguley, 1982; Zimmer & Wähnert, 1986; Portugal & Waring, 1987; Laughton, Jenkins, Fox & Neidle, 1990). We have shown that the molecular structure of berenil incorporates the concave surface typical of DNA minor groove binders (Pearl, Skelly, Hudson & Neidle, 1987). Molecular-modelling studies have produced low-energy arrangements for binding to both alternating $(AT)_n$ and oligo.A_nT_n sequences with at least two contiguous AT base pairs (Gresh & Pullman, 1986; Pearl *et al.*, 1987; Gago, Reynolds & Richards, 1989; Laughton *et al.*, 1990; Jenkins, Laughton & Neidle, to be published). These models have the terminal amidinium groups of the diprotonated ligand molecule acting as hydrogen-bond donors to either the O2 atom of thymine or the N3 atom of adenine. A recent crystal structure of berenil complexed with the sequence d(CGCGAATTCGCG)$_2$ has revealed that the ligand interacts with AT base pairs in a B-DNA minor groove (Brown *et al.*, 1990). NMR studies of the interaction of berenil with the same duplex have confirmed that the molecule forms a stable 1:1 complex in aqueous solution which involves recognition of the 5'-ATT sequence *via* the minor groove (Lane, Jenkins, Brown & Neidle, 1991).

We are currently exploiting the information derived from these models in attempts to modulate and perhaps switch the selectivity of berenil analogues from AT to GC. In this paper we report the crystal structures of two such analogues (Fig. 1) where the amidinium moieties have been replaced by carbonyl groups that can in principle accept hydrogen bonds from, for example, the minor groove exocyclic N2 amino group of a guanine base. These are the diketone derivative, 1,3-bis(4-acetylphenyl)-triazene (II) and the diester compound, 1,3-bis{4-

[2-(dimethylamino)ethoxycarbonyl]phenyl}triazene (III). The molecular structures obtained here provide important geometric parameters for molecular modelling. In this respect, we have examined the potential recognition properties of (II) and (III) with GC-containing oligonucleotides using a molecular-mechanics approach. This study, together with solution DNA binding data for these and other novel 1,3-diaryltriazenes, will be reported elsewhere.

Experimental

The two novel 1,3-diphenyltriazene compounds (Fig. 1) were recrystallized from aqueous ethanol: (II) crystallized as deep-orange plates, whilst (III) formed yellow plates. Preliminary X-ray data were obtained with Weissenberg and oscillation cameras. Accurate cell dimensions were obtained by least-squares refinement of 25 θ values measured on an Enraf–Nonius CAD-4 diffractometer. Crystal quality for compound (III) was poor, with high mosaic spread being apparent. Table 1 details the crystal data obtained for (II) and (III).

Intensity data for both compounds were collected at ambient temperature using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å), an ω–2θ scan technique and a maximum scan time of 120 s per reflection. In the case of (III), a larger than normal scan angle of $(1.15 + 0.142\tan\theta)^\circ$ was used. Intensity-standard reflections were monitored after every 60 min of X-ray exposure during the data collections.

The structures were solved by direct methods using *MULTAN*82 (Main *et al.*, 1982) for (II), and *SHELX*76 (Sheldrick, 1976) for (III). Full least-squares refinement of the scale factor and positional and anisotropic thermal parameters for non-H atoms was carried out using the Enraf–Nonius *SDP* package (Frenz, 1980). Some H atoms in both structures were located from difference Fourier syntheses and the remainder were calculated using standard geometric criteria. The H-atom positions and isotropic thermal parameters in structure (II) were included in the final stages of its refinement. All H atoms were kept fixed during the refinement of (III) and were assigned isotropic (B) thermal parameters 0.5 Å^2 greater than those of their bonded atoms. No

(I) X = -C(NH$_2$)$_2^+$

(II) X = -COCH$_3$
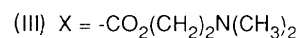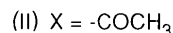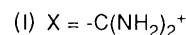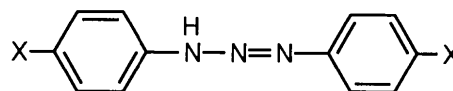
(III) X = -CO$_2$(CH$_2$)$_2$N(CH$_3$)$_2$

Fig. 1. Formulae of berenil (I) and triazenes (II), (III).

Table 1. *Details of data collections and structure refinements*

	(II)	(III)
(a) Data collection		
Crystal dimensions (mm)	0·50 × 0.50 × 0·05	0·30 × 0·15 × 0·04
Number, θ range of reflections ( )	25, 14–26	25, 7–26
Range h	0 to 15	−10 to 10
k	0 to 13	13 to 13
l	9 to 9	0 to 13
Maximum θ value ( )	67	60
Number. variation (%) of standard reflections	2, ± 5	3, ± 4
Number of intensity measurements	2802	3295
Number of unique reflections	2565	2939
Number of observed reflections	1890	1100
Criterion by which reflection judged observed	$F > 4\sigma(F)$	$F > 4\sigma(F)$
(b) Structure refinement		
R	0·089	0·063
wR	0·100	0·062
Weighting scheme	$1/[\sigma(F)^2 + 0·04 F]$	$1/[\sigma(F)^2 + 0·0005 F^2]$
$(\Delta \sigma)_{max}$ in final cycle	0·15	< 0·005
Max., min. heights in final ΔF map (e Å⁻³)	0·22, −0·24	0·28, 0·23

absorption corrections were applied in either structure. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

All computations were performed on VAX 11/750 and Alliant FX40/3 computers at the Institute of Cancer Research. Other details of the data collections and structure refinements are given in Table 1.

MNDO Hamiltonian calculations were performed on an Alliant FX40/3 computer using the *AMPAC* semi-empirical molecular-orbital package (Quantum Chemistry Program Exchange No. 506, Department of Chemistry, University of Indiana) with corrected parameter values for nitrogen (Stewart, 1989). Graphics visualization and modelling was carried out using the *GEMINI*1.03 (1990) molecular-modelling program on a Silicon Graphics IRIS 4D-20G work-station.

Discussion

Fig. 2 shows the molecular structures of the berenil derivatives (II) and (III). Fractional coordinates, bond lengths and angles are given in Tables 2 and 3.* Both structures have the linear triazene (N=N—NH) groups adopting an extended conformation with the 1,3-substituent phenyl rings arranged *cis* to each other. The same arrangement is observed for the parent compound, berenil (Pearl *et al.*, 1987). Both molecules here have approximately

* Tables of structure factors, anisotropic thermal parameters for non-H atoms and calculated H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53174 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coplanar phenyl rings, with interplanar dihedral angles of 4·6 (3)° for (II) and 3·7 (7)° for compound (III). The triazene group itself is not a fully delocalized system. Thus, the N1—N2 and N1'—N2 distances in both structures are non-equivalent, with mean values of 1·263 (3) and 1·335 (4) Å, respectively. This difference is highly significant, even though neither structure is of high accuracy. These distances, together with unequivocal location in both cases of the N1—H1 hydrogen atom, define the overall bonding arrangement to be essentially that shown in the structural formulae presented here. The C_{arom}—N1, C_{arom}—N1' and N—N bond lengths are comparable to those determined in the crystal structures of monoaryltriazenes (Kuroda & Wilman, 1985; Neidle, Pearl & Skelly, 1987). The N=N bond lengths in (II) and (III) are not significantly different from the average values for C_{arom}—N=N—C_{arom} of 1·240–1·255 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The consistent difference in length between the C1—N1 and C1'—N1' bonds of 0·03 Å is probably significant; for (II) this difference is > 7σ. In contrast to the present structures, the parent compound berenil (I) was found to lie on a crystallographic twofold axis, thus having statistical disorder (Pearl *et al.*, 1987).

The substituents at the C4 and C4' phenyl positions adopt very similar conformations in both structures, with the carbonyl oxygen atoms *trans* to each other. In the case of (II), the O1—C7—C4—C3 torsion angle is 4·1 (5)° with the equivalent O1'—C7'—C4'—C5' angle at the other end of the molecule being 172·3 (5)°. The corresponding torsion angles in (III) are −0·5 (10) and 175·7 (11)°, respectively. The existence of the *transoid* relationship
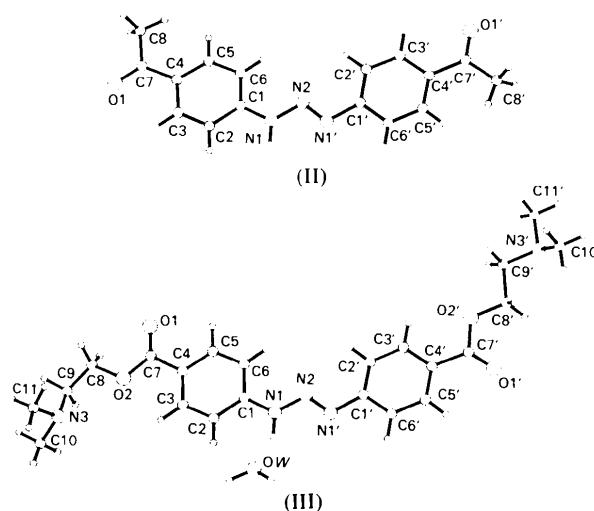

Fig. 2. Computer-drawn plots of the molecular structures of compounds (II) and (III).

Table 2. *Non-H-atom positional and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses, for compounds* (II) *and* (III)

The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation: $B_{iso} = (4/3)\sum_i \sum_j B_{ij}(\mathbf{a}_i.\mathbf{a}_j)$. O$W$ is a water molecule of crystallization.

	x	y	z	$B_{iso}(\text{Å}^2)$
Compound (II)				
C1	0.2587 (2)	0.0887 (2)	0.1438 (4)	4.0 (2)
C2	0.2093 (2)	0.0280 (2)	0.2476 (4)	4.2 (2)
C3	0.1530 (2)	0.0784 (2)	0.3459 (4)	4.1 (3)
C4	0.1431 (2)	0.1907 (2)	0.3486 (3)	4.0 (2)
C5	0.1954 (2)	0.2506 (3)	0.2481 (4)	4.4 (2)
C6	0.2519 (2)	0.2017 (3)	0.1465 (4)	4.5 (2)
C7	0.0771 (2)	0.2394 (3)	0.4551 (4)	4.5 (2)
C8	0.0619 (3)	0.3596 (3)	0.4476 (6)	5.6 (3)
C1'	0.4588 (2)	0.0738 (2)	-0.2533 (4)	4.1 (2)
C2'	0.4577 (3)	0.1850 (3)	-0.2839 (4)	4.9 (2)
C3'	0.5136 (2)	0.2262 (3)	-0.3923 (4)	4.9 (3)
C4'	0.5730 (2)	0.1596 (3)	-0.4726 (4)	4.2 (2)
C5'	0.5714 (2)	0.0491 (3)	-0.4433 (4)	4.3 (2)
C6'	0.5159 (2)	0.0075 (2)	-0.3349 (4)	4.4 (2)
C7'	0.6352 (2)	0.2074 (3)	-0.5848 (4)	4.6 (2)
C8'	0.6888 (3)	0.1361 (3)	-0.6871 (5)	5.8 (3)
N1	0.3116 (2)	0.0335 (2)	0.0399 (3)	4.5 (2)
N2	0.3604 (2)	0.0863 (2)	-0.0621 (3)	4.3 (2)
N1'	0.4048 (2)	0.0214 (2)	-0.1439 (3)	4.5 (2)
O1	-0.0367 (2)	0.1835 (2)	0.5451 (3)	5.9 (3)
O1'	0.6433 (2)	0.3064 (2)	0.5930 (4)	6.4 (3)
Compound (III)				
C1	0.1302 (7)	0.2945 (6)	0.7586 (5)	4.0 (2)
C2	0.0556 (7)	0.1804 (6)	0.8288 (5)	4.0 (2)
C3	0.0568 (7)	0.1547 (6)	0.8018 (5)	3.8 (2)
C4	-0.0961 (7)	0.2456 (6)	0.7029 (5)	4.3 (2)
C5	0.0238 (8)	0.3591 (7)	0.6371 (6)	5.7 (3)
C6	-0.0903 (8)	0.3851 (7)	0.6612 (6)	5.3 (2)
C7	0.2122 (7)	0.2231 (7)	0.6663 (6)	4.8 (2)
C8	-0.3812 (9)	0.0781 (9)	0.7009 (7)	8.3 (3)
C9	-0.421 (1)	-0.048 (1)	0.7697 (9)	24.7 (7)
C10	-0.582 (1)	-0.109 (1)	0.9615 (9)	18.4 (4)
C11	-0.431 (1)	-0.247 (1)	0.9012 (9)	14.8 (5)
C1'	0.5173 (7)	0.5292 (6)	0.6876 (6)	4.4 (2)
C2'	0.5023 (7)	0.6309 (7)	0.5846 (5)	4.9 (2)
C3'	0.5946 (7)	0.7333 (6)	0.5262 (5)	4.7 (2)
C4'	0.7071 (7)	0.7357 (6)	0.5670 (5)	4.1 (2)
C5'	0.7263 (7)	0.6324 (7)	0.6654 (6)	4.9 (2)
C6'	0.6304 (8)	0.5311 (6)	0.7261 (6)	5.0 (2)
C7'	0.8092 (8)	0.8451 (6)	0.5096 (5)	4.1 (2)
C8'	0.8725 (7)	1.0516 (7)	0.3540 (6)	5.0 (2)
C9'	0.8141 (7)	1.1488 (7)	0.2553 (6)	5.0 (2)
C10'	0.9470 (9)	1.3226 (7)	0.2227 (7)	7.2 (3)
C11'	0.8713 (9)	1.3318 (8)	0.0689 (7)	7.5 (3)
N1	0.2438 (6)	0.3151 (5)	0.7896 (4)	4.4 (2)
N2	0.3309 (6)	0.4174 (5)	0.7180 (4)	4.4 (2)
N3	0.4422 (6)	0.1184 (5)	0.8843 (5)	5.6 (2)
N1'	0.4270 (6)	0.4193 (5)	0.7605 (5)	4.8 (2)
N3'	0.9244 (6)	1.2478 (5)	0.1688 (4)	5.2 (2)
O1	-0.2492 (5)	0.3000 (5)	0.5816 (4)	7.6 (2)
O2	0.2691 (5)	0.1065 (4)	0.7342 (4)	6.3 (2)
O1'	0.9124 (5)	0.8475 (5)	0.5383 (4)	6.9 (2)
O2'	0.7728 (5)	0.9438 (4)	0.4175 (4)	5.0 (1)
OW'	0.1982 (5)	0.1509 (4)	1.0347 (3)	5.4 (1)

between the two carbonyl groups in each structure suggests that the energy barrier to rotation about the aryl—carbonyl (C4—C7 and C4'—C7') bonds is not high, and that there are two low-energy conformations separated by $\sim 180°$ so that in each instance the carbonyl group is approximately coplanar with, and conjugated to, the phenyl ring. The high temperature factors in (III) for atoms C9, C10 and C11 are suggestive of high motion or disorder within this part of the molecule; there was no evidence for discrete alternative conformations in the difference maps.

Table 3. *Intramolecular bond lengths* (Å) *and bond angles* (°), *with e.s.d.'s in parentheses, for compounds* (II) *and* (III)

	(II)	(III)		(II)	(III)
C1—C2	1.395 (4)	1.383 (9)	N1'—C1'	1.415 (4)	1.420 (8)
C2—C3	1.359 (4)	1.380 (12)	N1'—N2	1.267 (4)	1.260 (10)
C3—C4	1.395 (4)	1.398 (9)	C1'—C2'	1.398 (4)	1.384 (8)
C4—C5	1.394 (4)	1.367 (10)	C2'—C3'	1.368 (4)	1.371 (10)
C4—C7	1.488 (4)	1.481 (12)	C3'—C4'	1.398 (4)	1.388 (12)
C5—C6	1.371 (4)	1.371 (13)	C4'—C5'	1.389 (4)	1.366 (8)
C6—C1	1.400 (4)	1.385 (9)	C4'—C7'	1.480 (4)	1.493 (10)
C7—C8	1.501 (5)		C5'—C6'	1.366 (4)	1.380 (10)
C7—O1	1.213 (4)	1.209 (8)	C6'—C1'	1.382 (4)	1.370 (12)
C7—O2	–	1.336 (8)	C7'—C8'	1.493 (4)	
C8—C9	–	1.38 (2)	C7'—O1'	1.232 (4)	1.195 (10)
C8—O2	·	1.452 (13)	C7'—O2'		1.355 (7)
C9—N3		1.317 (11)	C8'—C9'	–	1.510 (10)
C10—N3	–	1.337 (10)	C8'—O2'	–	1.456 (8)
C11—N3		1.411 (15)	C9'—N3'	–	1.456 (8)
N1—C1	1.389 (4)	1.397 (11)	C10'—N3'	–	1.455 (13)
N1—N2	1.329 (3)	1.339 (7)	C11—N3'	·	1.457 (10)
N1—N2—N1'	111.2 (3)	111.7 (5)	N2—N1'—C1'	113.4 (3)	112.5 (5)
N2—N1—C1	121.2 (3)	120.8 (5)	N1'—C1'—C2'	125.1 (3)	127.0 (8)
N1—C1—C2	118.0 (3)	118.3 (6)	N1'—C1'—C6'	115.8 (3)	114.5 (5)
N1—C1—C6	122.8 (3)	121.9 (6)	C2'—C1'—C6'	119.0 (3)	118.5 (6)
C2—C1—C6	119.2 (3)	119.8 (8)	C1'—C2'—C3'	119.6 (3)	120.3 (8)
C1—C2—C3	120.0 (3)	120.8 (6)	C2'—C3'—C4'	121.4 (3)	120.9 (6)
C2—C3—C4	122.1 (3)	119.4 (6)	C3'—C4'—C5'	118.0 (3)	118.6 (7)
C3—C4—C5	117.3 (3)	118.6 (8)	C4'—C5'—C6'	120.8 (3)	120.4 (8)
C4—C5—C6	121.8 (3)	122.6 (6)	C1'—C6'—C5'	121.0 (3)	121.2 (6)
C1—C6—C5	119.6 (3)	118.7 (6)	C3'—C4'—C7'	120.0 (3)	123.8 (5)
C3—C4—C7	118.8 (3)	122.5 (6)	C5'—C4'—C7'	121.9 (3)	117.6 (7)
C5—C4—C7	123.9 (3)	118.9 (6)	C4'—C7'—C8'	120.3 (3)	--
C4—C7—C8	118.0 (3)		C4'—C7'—O1'	119.8 (3)	125.5 (6)
C4—C7—O1	120.9 (3)	124.0 (6)	C4'—C7'—O2'	–	111.7 (7)
C4—C7—O2		113.1 (6)	O1'—C7'—C8'	119.9 (3)	-
O1—C7—C8	121.1 (3)		O1'—C7'—O2'	–	122.8 (6)
O1—C7—O2		122.8 (6)	C7'—O2'—C8'		114.5 (6)
C7—O2—C8		115.6 (6)	O2'—C8'—C9'	–	106.0 (7)
O2—C8—C9		110.3 (8)	C8'—C9'—N3'	–	111.0 (6)
C8—C9—N3	-	130.0 (1)	C9'—N3'—C10'	–	112.0 (6)
C9—N3—C10	-	116.1 (7)	C9'—N3'—C11'	–	109.3 (6)
C9—N3—C11	·	107.0 (1)	C10'—N3'—C11'	–	109.7 (6)
C10—N3—C11		102.5 (7)			

MNDO calculations on the all-planar 1,3-diphenyltriazene core of the molecules reveal that rotation about the N1—N2 bond strongly favours the geometry found in the crystal state, with the phenyl rings adopting an extended *cis* arrangement. Calculations of enthalpy of formation (ΔH_f) for rotation about N1'—N2—N1—C1 show (Fig. 3) that this conformation is ~ 150 kJ mol^{-1} lower in energy than for the alternative *trans* orientation. However, MNDO calculations on the geometry-optimized *cis* and *trans* rotamers of 1,3-diphenyltriazene, where self-consistent fields were each achieved with final convergence to ≤ 5 J mol^{-1} and a final energy gradient of ≤ 10 J mol^{-1} Å^{-1}, reveal that the enthalpic barrier to rotation is reduced to only ≤ 3.3 kJ mol^{-1} once torsional constraints about the triazene linkage are relaxed. The averaged bond lengths determined for N1'—Cl', N1—N2 and N1'—N2 in the optimized molecules using this procedure (1.43, 1.35 and 1.24 Å, respectively) are also similar to those found in the crystal structures for (II) and (III). However, the bond length determined for N1—Cl (1.44 Å) is significantly different from that revealed in the present crystal structures.

The crystal structure analyses for these two berenil analogues have confirmed and extended the original structural data for the parent compound. The overall shape of the core 1,3-diaryltriazene residue is conserved, forming a concave surface which is suitable for complementary interaction with the convex surface of a B-DNA minor groove. A *cisoid* arrangement of carbonyl groups, with both hydrogen-bond acceptor moieties oriented toward the concave edge of the molecule, would optimize such interactions. The low energy barrier to rotation inferred suggests that both (II) and (III) may interact simultaneously with two (non-adjacent) hydrogen-bond-donating guanosine residues in a DNA sequence. This has indeed been found to be the case (Jenkins, Neidle, Bailly & Waring, to be published).

Compound (III) has the water molecule in its asymmetric unit hydrogen bonded to N1 of the triazene moiety, with its attached hydrogen atom H1 donating to the oxygen atom of the water molecule. The N1$\cdots$OW and H1$\cdots$OW distances are 2·83 (6) and 1·90 (6) Å, respectively, and the N1—H1$\cdots$OW angle formed is 152·9 (15)°. The two hydrogen atoms of the water are oriented away from the triazene group (Fig. 2). This arrangement provides further evidence for both a non-delocalized geometry and the location of the hydrogen associated with the triazene (N=N—NH) linkage in berenil and its derivatives. An identical water arrangement has been found by us in the crystal structure of a berenil–dodecanucleotide complex (Brown *et al.*, 1990), although not resolved in a recent NMR solution study of the same complex (Lane *et al.*, 1991).
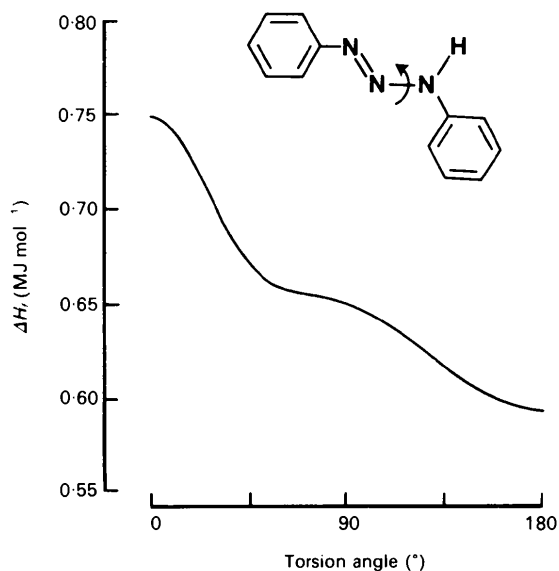
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Fig. 3. Calculated enthalpy of formation (ΔH_f) for initially all-planar 1,3-diphenyltriazene with variation of the N1'—N2—N1—C1 torsion angle.