

**(E)-4-(4-Bromophenyldiazenyl)-
2,6-dimethylphenyl acrylate and
(E)-2,6-dimethyl-4-(4-methylphenyl-
diazenyl)phenyl acrylate**Hasan Kocaokutgen,^a Ibrahim Uçar,^{b*} Mahmut Gür,^a
Sevil Özkınalı^a and Orhan Büyükgüngör^b^aDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey, and ^bDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey
Correspondence e-mail: iucar@omu.edu.tr

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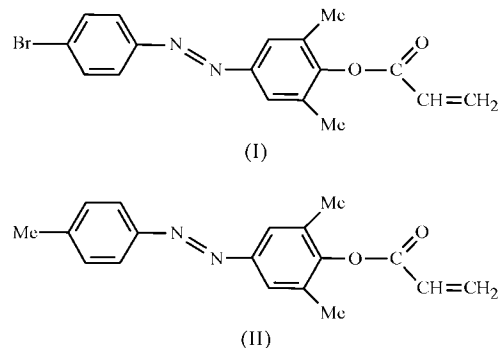
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The crystal structures of the title compounds, C₁₇H₁₅BrN₂O₂, (I), and C₁₈H₁₈N₂O₂, (II), determined at room temperature, have a *trans* configuration with respect to the diazene linkage, as found for other azo (diazene) derivatives. The aromatic mean planes are nearly coplanar, with a dihedral angle between these planes of 8.31 (2)° for (I) and 3.74 (2)° for (II). In both complexes, the mean plane of the ester group is nearly perpendicular to the aromatic ring planes. In both compounds, the crystal packing involves only π - π and π -ring interactions, which combine to stabilize the extended structure.

Comment

Aromatic azo compounds represent the dominant class of synthetic colourants (Peter & Freeman, 1991); they are the most widely used class of dyes because of their versatile application in various fields, such as the dyeing of textiles and fibres, as colourants in printing, and in high-technology areas, such as ink-jet printers (Catino & Farris, 1985). The reversible interconversion of the *cis* and *trans* isomers of azo compounds allows the use of these compounds in optical data storage and switching devices (Jeon *et al.*, 2002; Tian *et al.*, 2004). Such optical properties depend not only on the spectroscopic properties of the molecules but also on their crystallographic arrangement (Biswas & Umamathy, 2000). There is also interest in their biochemical applications because of their ability to bind to proteins (Ojala *et al.*, 1996). In our ongoing research on azo compounds, in order to provide templates for molecular modelling studies, we have synthesized some diazene derivatives, and the crystal structures of the title compounds, (I) and (II) (Figs. 1 and 2), have been determined. Both compounds crystallize in the centrosymmetric space group *P1*; therefore, the optical frequency-doubling (or second-harmonic generation) in non-linear optics does not

occur in the solid state. This process can occur only in non-centrosymmetric crystals.



The bond lengths and angles in both structures are within the normally expected ranges. Both structures have a *trans* configuration about the azo linkage with a nearly planar geometry [the torsion angle of the central -C-N=N-C- unit is 179.0 (2)° for (I) and 178.2 (3)° for (II)] and with C2-C1-N1=N2 and C13-C12-N2=N1 torsion angles of 0.5 (4) and -174.5 (3)°, respectively, in (I), and 2.0 (5) and 177.2 (4)° in (II). These torsion angles suggest delocalization of electron density between the aromatic rings and the azo group. However, the ester and the two methyl groups will probably cause the acryloyloxy group to rotate out of conjugation with the benzene ring, thus leading to a loss of planarity. The dihedral angle between the aromatic rings is 8.31 (2)° in (I) and 3.74 (2)° in (II).

The ester mean planes of (I) and (II) are approximately planar, with r.m.s. deviations of 0.0240 and 0.0148 Å; the largest deviations from the mean planes are 0.037 (3) and 0.025 (4) Å, respectively, for atom C10. The mean planes of the ester groups are nearly perpendicular to the aromatic rings, as indicated by the dihedral angles of 89.6 (1) and 82.7 (1)° in (I), and 88.1 (2) and 87.8 (2)° in (II). The N1-C1 and N2-C12 bond lengths are 1.428 (3) and 1.423 (3) Å, respectively, for (I), and 1.443 (4) and 1.446 (4) Å for (II), consistent with the conventional single C-N bond length (1.450 Å). Comparing the N2-C12 bond distances in the two compounds, we find that the N2-C12 bond in (I) is slightly shorter than that in (II), as a result of the presence of the Br atom in a *para* position with respect to the azo linkage. This result can be attributed to the electron-withdrawing groups attached to the benzene ring.

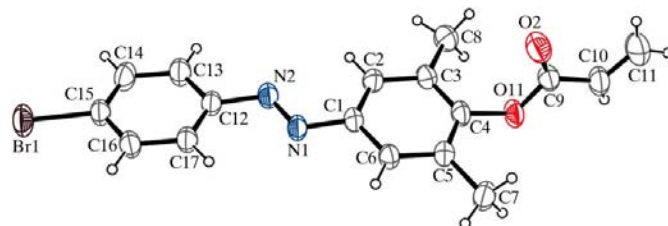


Figure 1
An ORTEP-3 (Farrugia, 1997) view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

The N=N bond lengths [N1=N2 = 1.252 (3) Å for (I) and 1.241 (4) Å for (II)] in both compounds are indicative of significant double-bond character, as has been observed in other *trans*-azo compounds (Kocaokutgen *et al.*, 2003; Soylu *et al.*, 2004). The C–Br bond distance in (I) is consistent with that in 2-[(*E*)-3-[(*E*)-4-bromophenyliminomethyl]-4-hydroxyphenyldiazenyl]benzoic acid toluene hemisolvate (Linden *et al.*, 2006) and (*E*)-5-(4-bromophenyldiazenyl)salicylaldehyde (Şahin *et al.*, 2005). The O2=C9 bond distance in both compounds is consistent with the value of the C=O double bond in other ester compounds (Kocaokutgen *et al.*, 2005).

In the extended structures of (I) and (II), there are no intra- or intermolecular hydrogen-bonding interactions. The crystal packing of (I) features π – π and π –ring interactions, which form supramolecular motifs extending along the crystallographic *a* axis (Fig. 3), while in (II), the crystal packing comprises only π – π interactions (Fig. 4). An intermolecular π – π contact occurs between the two symmetry-related aromatic rings (C1–C6 is ring *A* and C12–C17 is ring *B*) of neighbouring azo molecules. Rings *A* and *B* are oriented in such a way that the perpendicular distance from *A* to *B*ⁱ is 3.310 Å for (I) [symmetry code: (i) 1 + *x*, *y*, *z*] and 3.529 Å for (II), the closest interatomic distance is C3··C12ⁱ [3.466 (4) Å] for (I) and C2··C13ⁱ [3.564 (5) Å] for (II), and the dihedral angle between the planes of the rings is 8.31 (2)° for (I) and 3.74 (2)° for (II). The distance between the ring centroids is 3.857 (2) Å for (I) and 3.756 (2) Å for (II). Ring *A* is also involved in an intermolecular C–H·· π interaction with atom C10 of the ester group in (I). The distance between atom H10

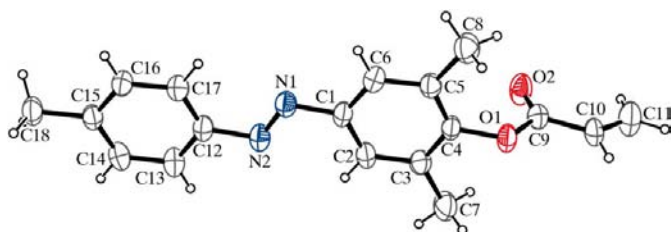


Figure 2
An ORTEP-3 (Farrugia, 1997) view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

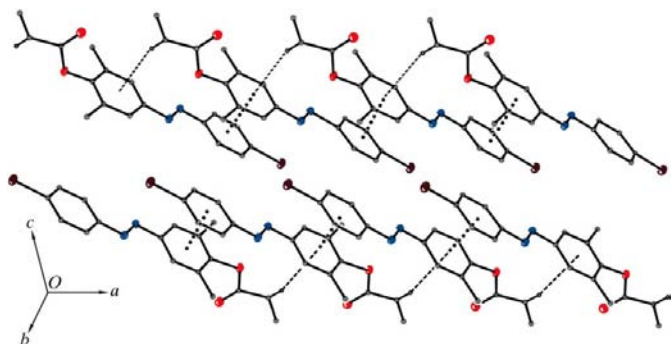


Figure 3
A packing diagram for (I), showing molecules linked by π – π and π –ring interactions between the aromatic rings.

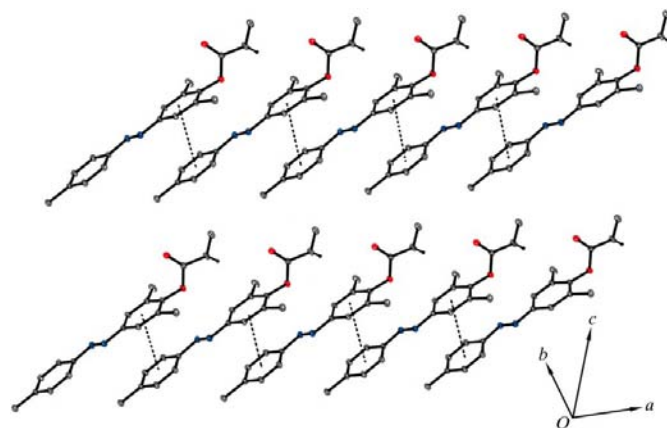


Figure 4
A packing diagram for (II), showing molecules linked by π – π interactions between the aromatic rings.

and the centre of ring *A* (*CgA*) is 2.90 Å, the distance between atom H10 and the plane of ring *A* is 2.90 Å, and the C10–H10··*CgA*ⁱ angle is 165°. In both complexes, a three-dimensional network is constructed from van der Waals forces between parallel associations formed by π – π and π –ring interactions. There is strong short contact between atoms C17 and C17ⁱⁱ for (I) [C17··C17ⁱⁱ = 3.685 (4) Å; symmetry code: (ii) –*x*, –*y*, 1 – *z*], and between atoms O2 and C18ⁱⁱⁱ for (II) [O2··C18ⁱⁱⁱ = 3.570 (5) Å; symmetry code: (iii) *x* + 1, *y*, *z* + 1].

Experimental

For the syntheses of azo–ester compounds containing an acryloyloxy group, first the derivatives of 4-hydroxyazobenzene dyes are prepared by the usual azo-coupling reaction of 2,6-dimethylphenol with substituted aryldiazonium salts, and then their acryloyloxy derivatives are synthesized in a Schotten–Bauman-type reaction similar to the following procedure and by a method described previously (Kocaokutgen *et al.*, 2005). To a stirred tetrahydrofuran solution (20 ml) of substituted 4-hydroxyazobenzene dye (2.48 mmol) and sodium metal (2.48 mmol), acryloyl chloride (2.48 mmol) was added dropwise under an atmosphere of dry nitrogen. After 2 h of stirring, the mixture was filtered and the desired product was precipitated out by adding water. The solid isolated by filtration was washed several times with water and then dried. The products were crystallized from an ethanol–water mixture to give related compounds. The products were crystallized from dimethyl sulfoxide to produce crystals of suitable quality for X-ray diffraction analysis.

Compound (I)

Crystal data

C₁₇H₁₅BrN₂O₂
M_r = 359.21
 Triclinic, *P* $\bar{1}$
a = 6.2168 (10) Å
b = 9.7823 (10) Å
c = 14.0973 (7) Å
 α = 98.977 (3)°
 β = 101.160 (2)°
 γ = 93.697 (7)°

V = 826.83 (16) Å³
Z = 2
D_x = 1.443 Mg m^{–3}
 Mo *K* α radiation
 μ = 2.49 mm^{–1}
T = 297 (2) K
 Prism, orange
 0.4 × 0.3 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer	14480 measured reflections
ω scans	3931 independent reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	2667 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.975$, $T_{\max} = 0.987$	$R_{\text{int}} = 0.056$
	$\theta_{\text{max}} = 27.9^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.2083P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{Å}^{-3}$
3931 reflections	$\Delta\rho_{\text{min}} = -0.41 \text{ e } \text{Å}^{-3}$
201 parameters	
H-atom parameters constrained	

Compound (II)

Crystal data

$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$	$V = 835.13 (19) \text{ Å}^3$
$M_r = 294.34$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.171 \text{ Mg m}^{-3}$
$a = 6.1589 (8) \text{ Å}$	Mo $K\alpha$ radiation
$b = 11.2603 (15) \text{ Å}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 12.3461 (16) \text{ Å}$	$T = 297 (2) \text{ K}$
$\alpha = 82.780 (11)^\circ$	Prism, orange
$\beta = 80.070 (11)^\circ$	$0.23 \times 0.21 \times 0.16 \text{ mm}$
$\gamma = 85.321 (11)^\circ$	

Data collection

Stoe IPDS-II diffractometer	10895 measured reflections
ω scans	3298 independent reflections
Absorption correction: integration <i>X-RED32</i> (Stoe & Cie, 2002)	1615 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.980$, $T_{\max} = 0.985$	$R_{\text{int}} = 0.144$
	$\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.315P]$
$R[F^2 > 2\sigma(F^2)] = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.216$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.13 \text{ e } \text{Å}^{-3}$
3298 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{Å}^{-3}$
206 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.018 (5)

Crystals of (II) gave a low mean data intensity, so the proportion of the data labelled 'observed' is rather low (49%). In both compounds,

all H atoms attached to C atoms were refined using a riding model [$\text{C}-\text{H} = 0.93 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and $\text{C}-\text{H} = 0.96 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms], except for atom H10 in compound (II), which was located from a difference map after the other H atoms had been refined using the riding model.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3067). Services for accessing these data are described at the back of the journal.

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