

Table 2. Selected geometric parameters (Å, °)

O(1)—C(1)	1.196 (9)	C(21)—C(22)	1.400 (8)
O(2)—C(3)	1.224 (6)	C(22)—C(23)	1.356 (8)
N(1)—C(21)	1.369 (7)	C(23)—C(24)	1.391 (8)
N(1)—C(2)	1.451 (8)	C(24)—C(25)	1.398 (8)
N(2)—C(31)	1.372 (7)	C(25)—C(26)	1.385 (9)
N(2)—C(2)	1.459 (7)	C(31)—C(36)	1.390 (7)
C(1)—C(24)	1.45 (1)	C(31)—C(32)	1.406 (8)
C(1)—C(11)	1.49 (1)	C(32)—C(33)	1.370 (8)
C(3)—C(34)	1.454 (8)	C(33)—C(34)	1.404 (7)
C(3)—C(41)	1.503 (8)	C(34)—C(35)	1.401 (7)
C(11)—C(16)	1.33 (1)	C(35)—C(36)	1.380 (8)
C(11)—C(12)	1.37 (1)	C(41)—C(46)	1.378 (8)
C(12)—C(13)	1.39 (2)	C(41)—C(42)	1.389 (9)
C(13)—C(14)	1.35 (2)	C(42)—C(43)	1.37 (1)
C(14)—C(15)	1.31 (2)	C(43)—C(44)	1.37 (1)
C(15)—C(16)	1.40 (1)	C(44)—C(45)	1.35 (1)
C(21)—C(26)	1.392 (8)	C(45)—C(46)	1.39 (1)
C(21)—N(1)—C(2)	123.9 (5)	C(22)—C(23)—C(24)	122.5 (6)
C(31)—N(2)—C(2)	122.6 (5)	C(23)—C(24)—C(25)	117.7 (6)
O(1)—C(1)—C(24)	121.6 (9)	C(23)—C(24)—C(1)	123.4 (7)
O(1)—C(1)—C(11)	116.9 (8)	C(25)—C(24)—C(1)	118.9 (7)
C(24)—C(1)—C(11)	121.6 (7)	C(26)—C(25)—C(24)	120.3 (6)
N(1)—C(2)—N(2)	111.3 (5)	C(25)—C(26)—C(21)	121.0 (6)
O(2)—C(3)—C(34)	122.1 (6)	N(2)—C(31)—C(36)	119.9 (6)
O(2)—C(3)—C(41)	118.4 (6)	N(2)—C(31)—C(32)	121.7 (6)
C(34)—C(3)—C(41)	119.5 (6)	C(36)—C(31)—C(32)	118.5 (6)
C(16)—C(11)—C(12)	117 (1)	C(33)—C(32)—C(31)	119.9 (5)
C(16)—C(11)—C(1)	120 (1)	C(32)—C(33)—C(34)	122.3 (5)
C(12)—C(11)—C(1)	122 (1)	C(35)—C(34)—C(33)	117.1 (6)
C(11)—C(12)—C(13)	121 (1)	C(35)—C(34)—C(3)	123.6 (6)
C(14)—C(13)—C(12)	119 (1)	C(33)—C(34)—C(3)	119.3 (6)
C(15)—C(14)—C(13)	121 (1)	C(36)—C(35)—C(34)	121.0 (5)
C(14)—C(15)—C(16)	120 (1)	C(35)—C(36)—C(31)	121.2 (5)
C(11)—C(16)—C(15)	122 (1)	C(46)—C(41)—C(42)	118.5 (7)
N(1)—C(21)—C(26)	118.5 (6)	C(46)—C(41)—C(3)	122.8 (6)
N(1)—C(21)—C(22)	123.2 (6)	C(42)—C(41)—C(3)	118.6 (6)
C(26)—C(21)—C(22)	118.3 (6)	C(43)—C(42)—C(41)	121.0 (7)
C(23)—C(22)—C(21)	120.2 (6)		

The crystal was mounted in a random orientation on a glass fibre. Data were collected using *CONTROL* software (Molecular Structure Corporation, 1988). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983) and *DIRDIF* (Beurskens, 1984). The C, O and N atoms were located in an *E* map. H atoms were placed in geometrically calculated positions with C—H = 0.95 Å, but were not included in the refinement. Anomalous-dispersion corrections were not applied. All calculations were performed on a MicroVAX II computer using the *TEXSAN* (Molecular Structure Corporation, 1987) program package. Molecular graphics were produced using the *PLUTO* program (Motherwell & Clegg, 1976).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and a packing diagram of the unit cell have been deposited with the IUCr (Reference: LI1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-[4-(4-Bromobenzylideneamino)phenyl]-3-(4-bromophenyl)-2-propen-1-one

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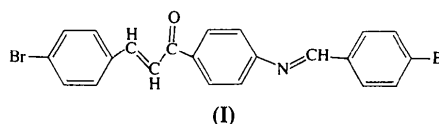
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Abstract

In the title compound, C₂₂H₁₅Br₂NO, the torsion angle O(1)—C(1)—C(2)—C(3) within the C₇H₇CO group is –21 (2)° and H atoms are in *trans* positions. The dihedral angles between the three phenyl rings are 46.2 (6), 168.2 (6) and 132.6 (6)°.

Comment

The chalcone derivatives are newly developed organic crystals with non-linear optical coefficients (Fichou, Watanabe, Takeda, Miyata, Goto & Nakayama, 1988). In order to explore the relationship between their structure and non-linear optical properties, we synthesized a series of substituted chalcones. The title compound, (I), is one of these, which happens to crystallize in a centrosymmetric space group and, therefore, has no non-linear optical properties. This has been confirmed by second harmonic generation (SHG) efficiency measurements on a powder sample using the method of Kurtz & Perry (1968).



The title compound was prepared by the condensation of *p*-bromobenzaldehyde and *p*-aminoacetophenone at room temperature, 10% aqueous NaOH solution being added as the condensation agent. The torsion angle O(1)—C(1)—C(2)—C(3) of the C₂H₂CO group is -21 (2)°. The H atoms are *trans* in the —C=C— group and the dihedral angles between phenyl rings are 46.2 (6), 168.2 (6) and 132.6 (6)°. It is significant that the degree of conjugation within the molecule is poor.

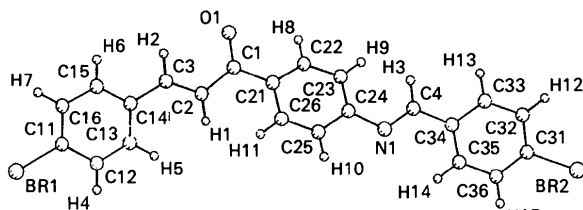


Fig. 1. The molecular structure of the title compound.

Experimental

Crystal data

C₂₂H₁₅Br₂NO

M_r = 469.17

Orthorhombic

Pbca

a = 44.04 (1) Å

b = 14.270 (5) Å

c = 5.891 (4) Å

V = 3702 (5) Å³

Z = 8

D_x = 1.68 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 20 reflections

θ = 9–11°

μ = 4.345 mm⁻¹

T = 294 K

Plate

1.0 × 0.4 × 0.1 mm

Light yellow

Crystal source: from ethanol solution

Data collection

Rigaku AFC-5R diffractometer

ω-2θ scans

Absorption correction:

empirical (DIFABS);

Walker & Stuart, 1983)

T_{min} = 0.30, *T_{max}* = 1.70

3785 measured reflections

3785 independent reflections

1364 observed reflections

[*I* > 3σ(*I*)]

Refinement

Refinement on *F*

R = 0.064

wR = 0.072

S = 1.64

1364 reflections

235 parameters

H-atom parameters not refined

θ_{max} = 25°

h = 0 → 17

k = 0 → 52

l = 0 → 7

3 standard reflections

monitored every 250

reflections

intensity variation: 0.3%

w = 1/σ²(*F_o*)

(Δ/σ)_{max} = 0.02

Δρ_{max} = 0.68 e Å⁻³

Δρ_{min} = -0.74 e Å⁻³

Atomic scattering factors from Cromer & Waber (1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Br(1)	0.48865 (3)	0.3592 (1)	0.8392 (3)	4.49 (9)
Br(2)	0.04469 (3)	0.3492 (1)	1.1013 (3)	5.0 (1)
O(1)	0.3285 (2)	0.3735 (6)	1.754 (2)	4.3 (6)
N(1)	0.1997 (3)	0.3699 (7)	1.250 (2)	3.2 (6)
C(1)	0.3226 (3)	0.3755 (9)	1.547 (2)	2.4 (7)
C(2)	0.3466 (3)	0.3712 (8)	1.378 (2)	2.6 (7)
C(3)	0.3748 (3)	0.3930 (9)	1.427 (2)	2.5 (6)
C(4)	0.1780 (3)	0.3956 (9)	1.378 (2)	2.8 (7)
C(11)	0.4536 (3)	0.3723 (8)	1.017 (2)	2.3 (6)
C(12)	0.4257 (3)	0.3376 (8)	0.932 (3)	2.6 (6)
C(13)	0.4004 (2)	0.3471 (8)	1.065 (2)	1.9 (6)
C(14)	0.4016 (3)	0.3881 (8)	1.283 (2)	1.8 (6)
C(15)	0.4288 (3)	0.4202 (8)	1.355 (2)	2.8 (7)
C(16)	0.4548 (3)	0.4117 (9)	1.230 (2)	2.7 (7)
C(21)	0.2908 (3)	0.3748 (8)	1.474 (2)	1.9 (6)
C(22)	0.2674 (3)	0.3416 (8)	1.613 (2)	2.9 (7)
C(23)	0.2375 (3)	0.3411 (9)	1.552 (2)	2.5 (6)
C(24)	0.2292 (3)	0.3735 (9)	1.340 (3)	2.7 (7)
C(25)	0.2517 (3)	0.4070 (9)	1.192 (2)	2.7 (7)
C(26)	0.2817 (3)	0.4067 (9)	1.257 (2)	2.5 (7)
C(31)	0.0858 (3)	0.3672 (8)	1.180 (2)	2.9 (7)
C(32)	0.0920 (3)	0.4051 (9)	1.383 (2)	2.8 (7)
C(33)	0.1226 (3)	0.4154 (9)	1.445 (2)	3.0 (8)
C(34)	0.1465 (3)	0.3868 (8)	1.303 (2)	2.0 (6)
C(35)	0.1383 (3)	0.3476 (9)	1.098 (2)	3.0 (7)
C(36)	0.1085 (3)	0.3383 (8)	1.033 (2)	2.7 (7)

Table 2. Selected geometric parameters (Å, °)

Br(1)—C(11)	1.87 (1)	C(14)—C(15)	1.35 (2)
Br(2)—C(31)	1.89 (1)	C(15)—C(16)	1.37 (2)
O(1)—C(1)	1.25 (1)	C(21)—C(22)	1.40 (2)
N(1)—C(4)	1.27 (2)	C(21)—C(26)	1.42 (2)
N(1)—C(24)	1.41 (1)	C(22)—C(23)	1.37 (2)
C(1)—C(2)	1.45 (2)	C(23)—C(24)	1.38 (2)
C(1)—C(21)	1.47 (2)	C(24)—C(25)	1.41 (2)
C(2)—C(3)	1.31 (2)	C(25)—C(26)	1.38 (2)
C(3)—C(14)	1.46 (2)	C(31)—C(32)	1.34 (2)
C(4)—C(34)	1.46 (2)	C(31)—C(36)	1.38 (2)
C(11)—C(16)	1.37 (2)	C(32)—C(33)	1.40 (2)
C(11)—C(12)	1.42 (2)	C(33)—C(34)	1.40 (2)
C(12)—C(13)	1.37 (2)	C(34)—C(35)	1.38 (2)
C(13)—C(14)	1.41 (2)	C(35)—C(36)	1.37 (2)
C(4)—N(1)—C(24)	117 (1)	C(26)—C(21)—C(1)	122 (1)
O(1)—C(1)—C(2)	121 (1)	C(23)—C(22)—C(21)	124 (1)
O(1)—C(1)—C(21)	119 (1)	C(22)—C(23)—C(24)	119 (1)
C(2)—C(1)—C(21)	120 (1)	C(23)—C(24)—C(25)	119 (1)
C(3)—C(2)—C(1)	122 (1)	C(23)—C(24)—N(1)	125 (1)
C(2)—C(3)—C(14)	129 (1)	C(25)—C(24)—N(1)	115 (1)
N(1)—C(4)—C(34)	121 (1)	C(26)—C(25)—C(24)	120 (1)
C(16)—C(11)—C(12)	120 (1)	C(25)—C(26)—C(21)	122 (1)
C(16)—C(11)—Br(1)	121 (1)	C(32)—C(31)—C(36)	122 (1)
C(12)—C(11)—Br(1)	119 (1)	C(32)—C(31)—Br(2)	118 (1)
C(13)—C(12)—C(11)	118 (1)	C(36)—C(31)—Br(2)	120 (1)
C(12)—C(13)—C(14)	122 (1)	C(31)—C(32)—C(33)	118 (1)
C(15)—C(14)—C(13)	117 (1)	C(32)—C(33)—C(34)	122 (1)
C(15)—C(14)—C(3)	121 (1)	C(35)—C(34)—C(33)	116 (1)
C(13)—C(14)—C(3)	121 (1)	C(35)—C(34)—C(4)	123 (1)
C(14)—C(15)—C(16)	123 (1)	C(33)—C(34)—C(4)	120 (1)
C(15)—C(16)—C(11)	120 (1)	C(36)—C(35)—C(34)	122 (1)
C(22)—C(21)—C(26)	115 (1)	C(35)—C(36)—C(31)	119 (1)
C(22)—C(21)—C(1)	122 (1)		

The coordinates of the H atoms were added according to theoretical models and were included in the structure-factor calculations. All calculations were performed on a VAX computer with programs from the TEXSAN crystallographic software package (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: AS1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trinitromethane

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Abstract

The structure of cubic trinitromethane, CHN₃O₆, has been determined at 200 K. Warning: a severe explosion has been reported [Macbeth (1913). *Ber. Dtsch. Chem. Ges.* **46**, 2537–2539] during the preparation of a sodium trinitromethanide salt.

Comment

Trinitromethane is a strong hydrocarbon acid and readily forms a crystalline 2:1 adduct with dioxane, which exhibits the shortest C—H···O hydrogen bonds, with a C—O distance of only 2.94 Å (Bock, Dienelt, Schödel & Havlas, 1993), reported so far (Cambridge Structural Database, 1993; Desiraju, 1991; Taylor & Kennard, 1984). Relative to the average conformation of monomeric HC(NO₂)₃ in the gas phase as determined by electron diffraction (Sadova, Popik, Vilkov, Pankrushev & Shlyapochnikov, 1973), the only significant structural change observed in the solid hydrogen-bridged dioxane

aggregate is an increase in the mean torsion angle $\omega(\text{H—C—N—NO}_2)$ from 26 to 47°. *Ab initio* self-consistent field (SCF) calculations (Cioslowski, Mixon & Fleischmann, 1991) reproduce satisfactorily the experimental structural data and predict torsion angles of 46–48° for the molecular skeleton of approximately C₃ symmetry. This is confirmed for liquid trinitromethane by infrared and Raman spectroscopic studies (Brookes & Jonathan, 1968). The following thermodynamic values have been measured for trinitromethane (Miroshnichenko, Lebedev, Sheveleo & Gulivskajo, 1967): heat of combustion 521 kJ mol⁻¹, heat of sublimation 46 kJ mol⁻¹ and heat of evaporation 33 kJ mol⁻¹. The single-crystal structure determination of HC(NO₂)₃ reported here was undertaken after the discovery of its hydrogen-bridged adduct with dioxane, during an attempted purification by recrystallization from ether solvents (Dienelt, 1993), resulting from the strong cation solvation properties of its anion [C(NO₂)₃]⁻. This was proved for ether solution (Bock, Hauck, Näther & Havlas, 1994) and by the isolation and structural characterization of the *aci*-diphenylnitromethane dimer (Bock, Dienelt, Schödel, Havlas, Herdtweck & Herrmann, 1993).

Fig. 1 shows an enlarged plot of 50% probability displacement ellipsoids. The molecular packing in the unit cell of trinitromethane is shown in the stereoscopic view in Fig. 2. The cubic unit cell contains eight formula units and the asymmetric unit comprises the HCNO₂ fragment. The molecular C₃ symmetry is verified by normal temperature ellipsoids of the NO₂ group (Fig. 1). The shortest intermolecular distances (C···O ≥ 3.16, N···O ≥ 2.95 Å) are outside the sum of the van der Waals radii and, unexpectedly (Bock, Dienelt, Schödel & Havlas, 1994), no C—H···O hydrogen bridges are formed. In the individual molecules, the N centre is planar (Table 1: sum of angles 127.0 + 117.7 + 115.3 = 360.0°) and the nitro group is rotated out of the HCN plane by 44°. The structure parameters determined for trinitromethane remain largely unchanged on hydrogen bonding to dioxane, (O₂N)₃CH···O(CH₂CH₂)₂O···HC(NO₂)₃, where only two rotational angles are slightly larger [by 2 and 9°, respectively (Bock, Dienelt, Schödel & Havlas, 1994)]. The experimental bond lengths and angles of the title molecule are satisfactorily reproduced by an *ab initio* SCF calculation (Cioslowski, Mixon & Fleischmann, 1991), providing additional evidence for the absence of specific intermolecular interactions within the crystal lattice (Fig. 2).

A tempting target for future crystal investigations would be the isolation of *aci*-trinitromethane [O₂N=C(NO₂)—N(O)OH]_n in close analogy to the recently crystallized and structurally characterized *aci*-diphenylnitromethane dimer [(H₅C₆)₂C=N(OH)₂—N=C(C₆H₅)₂] (Bock *et al.*, 1993).