N-{2-[(3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-phenyl}-N-(5,7-dinitroquinolin-8-yl)-1-phenylmethanesulfonamide: the nature of intramolecular shortened contacts

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The title compound, $C_{36}H_{35}N_5O_7S$, is found to exist in a non-spirocyclic (ring-opened) form in the crystal, although equilibrium of ring-opened and ring-closed forms (or so-called ring–chain isomerization) is possible in solution. The 4-oxocyclohexa-2,5-diene ring has a flattened sofa conformation. The N···C intramolecular separation of the atoms which would be directly bonded in a ring-closed form is quite short [2.813 (5) Å]. Topological analysis of charge density based on density-functional-theory calculations was used for consideration of shortened intramolecular contacts and indicates a strong attractive bonding interaction between these N and C atoms in the crystal structure.

Comment

It is well known that electron-deficient aromatic compounds containing a tropolone moiety or its heteroatomic analogues can undergo acylotropic rearrangement (Knyazev & Drozd, 1995; Kurbatov et al., 1997). This rearrangement usually includes reversible migration of the electron-deficient aryl group and proceeds through formation of a dipolar spirocyclic Meisenheimer complex with the tropylium cation. Several structures of such dipolar Meisenheimer complexes have been established using X-ray methods (Borbulevych, Antipin & Olekhnovich, 1999; Borbulevych, Shishkin et al., 1999; Furmanova et al., 1980; Olekhnovich, Furmanova et al., 1982). Basically, in solutions of such compounds, there is equilibrium between the ring-opened and ring-closed (Meisenheimer

complex) isomers, and interrelation of these forms is determined by many factors (Olekhnovich et al., 1994). However, not only tropolone derivatives exhibit this so-called ring–chain isomerization. In particular, equilibrium of the ring-opened and ring-closed forms occurs in solution for (1Z)-1-{[iso-propyl(2,4,6-trinitrophenyl)amino]methylene}-4a,8a-dihydro-naphthalen-2(1H)-one, and a dipolar spirocyclic isomer was found in the crystal phase (Olekhnovich, Mikhailov et al., 1982). Another example is the title compound, (I). According to preliminary NMR data (Borysenko et al., 1998), both ring-opened and ring-closed isomers of (I) are observed in solution (see scheme). Therefore, it is important to establish the structure of (I) in the crystal.

(I)
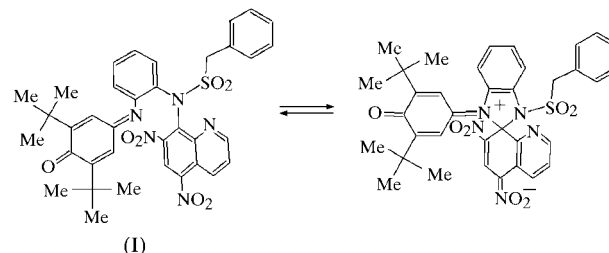
X-ray investigation has shown that the bond lengths in (I) do not differ considerably from standard values (Allen et al., 1987). The nitro groups in (I) are not coplanar with the quinoline moiety [the O2—N2—C5—C6 and O3—N3—C7—C6 torsion angles are −31.4 (6) and 52.7 (5)°, respectively], which is likely to be a result of the bulky substituent at atom C8.

Atom N4 has a planar conformation: the sum of the bond angles in the C10/S1/C8/N4 fragment is 359.5 (7)°. This fragment is rotated with respect to the fused-ring system and the angle between these two planes is 63.2 (1)°. The phenyl-methanesulfonyl group in (I) has an ac conformation with respect to the C7—C8 bond [the S1—N4—C8—C7 torsion angle is −116.4 (3)°].

The C10–C15 benzene ring is rotated with respect the C8—N4 bond and the corresponding C8—N4—C10—C11 torsion angle is 45.6 (5)°. The cyclohexa-2,5-dien-1-one fragment has an sc orientation with respect to the C11—C12 bond. The C23—N5—C11—C12 torsion angle is 63.0 (5)°. Unexpectedly, the C23–C28 dihydrocycle has a flattened sofa conformation and the deviation of atom C26 from the mean-squares plane of the other ring atoms is only −0.090 (6) Å, despite the presence of two tert-butyl groups. It was shown by Shishkin (1997) that similar partially hydrogenated rings with exocyclic double bonds possess high conformational flexibility, and the presence of bulky substituents often gives rise to distinct non-planar conformations of such rings. The steric strain in this fragment of (I) is confirmed by a number of shortened intra-molecular contacts, which are listed in Table 1. Nevertheless, nearly symmetrical steric interactions between the atoms of a dihydrocycle and several substituents could result in planarity of the ring (Borbulevych et al., 2000). Apparently, a similar situation occurs in (I), since the positions of the tert-butyl groups are symmetrical relative to the C23···C26 direction.

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Overall, in the crystal phase, compound (I) is found to be in the ring-opened form. But, clearly, the breakage and formation of the N5—C8 bond is a key stage of the ring-chain isomerization of (I); the distance between these two atoms [2.813 (5) Å] is shorter than the sum of the van der Waals radii of N and C (Table 2). However, it is impossible to reach any conclusion about the nature of this interaction based only on consideration of the distance between atoms N5 and C8. This interaction could be either a bonding or a non-bonding one.

To determine the nature of such intramolecular interactions, a topological analysis in the framework of Bader's 'atoms in molecules' (AIM) theory (Bader, 1990) was applied in the present study. According to this theory, the structure of a many-electron system with a given nuclear configuration R is completely determined by a set and types of critical points of the charge density $\rho(r,R)$ where the gradient of the charge density vanishes $[\nabla\rho(r) = 0]$. The second derivatives of $\rho(r)$ calculated at these points comprise a real symmetrical Hessian matrix and the eigenvalues of the Hessian determine the type of the critical point (Bader, 1990).

Critical points of the $(3,-1)$ type, or so-called bond critical points, which determine bonding interactions between two atoms of the molecular system, are of prime importance from the chemical standpoint. Their presence is a necessary condition for chemical bonding. It is believed that a bonding interaction occurs between two atoms if there is a line (bonding path) linking their nuclei along which the charge density has a maximum with respect to any lateral shift, and which has a minimum at the bond critical point $(3,-1)$. Such a $(3,-1)$ critical point in the region of the N5···C8 contact was revealed (Table 2). This indicates a strong attractive interaction between these atoms in the crystal of (I). In the AIM theory, this interaction is classified as a so-called interaction of closed shells, since the Laplacian of the charge density $\nabla^2\rho(r)$, which is determined as the sum of the eigenvalues of the Hessian, at this $(3,-1)$ critical point is positive. Moreover, a series of other shortened attractive intramolecular contacts characterized by $(3,-1)$ critical points has been found in (I) (Table 2); most of them are intramolecular C—H···O or C—H···N contacts.

It is of note that the values found for $\rho(r)$ in (I) (0.09–0.11 e Å^{-3}) at the critical points for intramolecular C—H···O contacts (Table 2) are twice as large as those for intermolecular hydrogen bonds studied previously (Koch & Popelier, 1995; Coppens et al., 1999; Borbulevych et al., 1998). It is likely that the four C—H···O interactions involving atom O7 of the carbonyl group in (I) favour planarity of the C23–C28 dihydrocycle.

For a long time, the van der Waals radii concept (Bondi, 1964; Zefirov & Zorky, 1989) has been a common approach for the consideration of non-bonded interactions. Moreover, it was suggested recently that mean statistical contacts (Rowland & Taylor, 1996) be used for this purpose. However, none of these approaches gives a valid conclusion about the nature of shortened contacts and, in general, attractive and repulsive interactions cannot be distinguished. On the other hand, the attractive bonding character of shortened contacts can be unambiguously established by topological analysis of the charge density, as has been demonstrated in the present study.
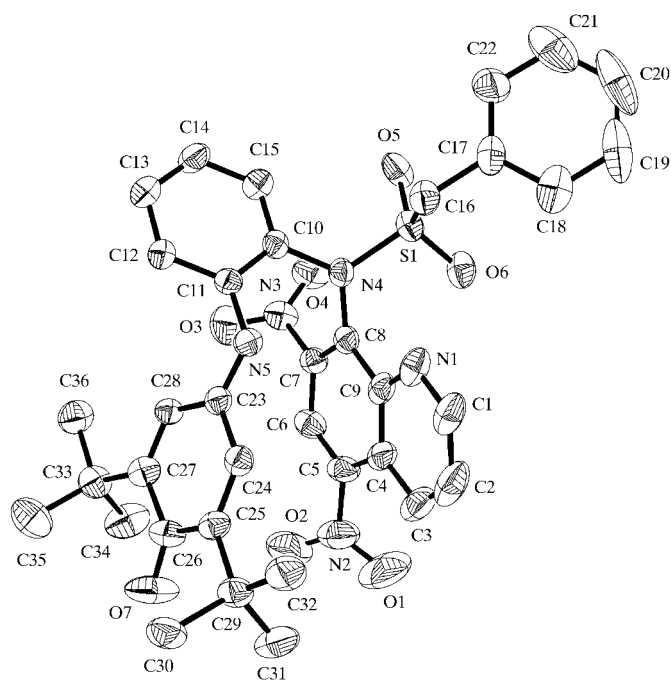

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Experimental

For the synthesis of (I), a mixture of the thallium salt (see below) of N-{2-[(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-phenyl}-1-phenylmethanesulfonamide, (II) (0.34 g, 0.5 mmol), 8-chloro-5,7-dinitroquinoline (0.13 g, 0.5 mmol), obtained according to Khilkova et al. (1992), and pyridine (0.049 g, 0.6 mmol) in acetonitrile (10 ml) was boiled for 30 min. The ThCl precipitate was filtered off and the filtrate was concentrated by evaporation. Compound (I) was separated by a chromatographic method. Red crystals of (I) of m.p. 508 K (decomposition) were obtained by recrystallization from 2-butanol (yield 18%, 0.06 g). The ^{1}H NMR spectrum of (I) was recorded using a Bruker DPX-250 spectrometer, with trimethyl sulfoxide as the internal standard. Spectroscopic analysis, ^{1}H NMR (acetone-d_6, 250 MHz, δ): 1.06 (s, 9H, ^{t}Bu at C25), 1.14 (s, 9H, ^{t}Bu at C33), 5.17 (d, 1H, CH$_2$, J = 13.1 Hz), 6.00 (d, 1H, CH$_2$, J = 13.2 Hz), 5.81 (d, 1H, H24, J = 2.5 Hz), 6.27 (d, 1H, H28, J = 2.5 Hz), 6.58 (dd, 1H H15, J = 7.7 and 1.5 Hz), 7.24–7.40 (m, 5H, Ph), 7.56–7.60 (m, 2H, H13, H14), 8.15 (dd, 1H, H12, J = 11.2 and 2.7 Hz), 8.18 (dd, 1H, H2, J = 8.8 and 4.0 Hz), 8.67 (s, 1H, H6), 9.04 (dd, 1H, H3, J = 8.8 and 1.5 Hz), 9.65 (dd, 1H, H1, J = 4.0 and 1.5 Hz). Compound (II) was obtained from the reaction between N-(2-aminophenyl)-1-phenyl-methanesulfonamide (3 g, 11.45 mmol; Olekhnovich et al., 1992) and 2,6-di-tert-butylbenzo-1,4-quinone (2.52 g, 11.45 mmol; Ley & Miller, 1956) in 2-propanol (50 ml). The mixture was boiled for 8 h and then cooled. After 12 h, the precipitate of (II) was filtered off. Compound (II) was purified by a chromatographic method and then recrystallized from i-amil alcohol. Red crystals of (II) were obtained

(m.p. 446 K; yield 62%, 3.3 g). For the preparation of the thallium salt of (II), compound (II) (0.26 g, 0.6 mmol) was added to a solution of KOH (0.4 g, 0.7 mmol) in methanol (20 ml) and a solution of thallium(I) acetate (0.18 g, 0.7 mmol) in methanol (5 ml) was added to the resulting solution. The mixture was stirred for 30 min, after which time the precipitate was filtered off and dried *in vacuo*. Violet crystals were obtained (m.p. 483 K; yield 97%, 0.36 g).

Crystal data

$C_{36}H_{35}N_5O_7S$	Mo $K\alpha$ radiation
$M_r = 681.75$	Cell parameters from 24
Orthorhombic, $P2_12_12_1$	reflections
$a = 12.227$ (4) Å	$\theta = 10–11°$
$b = 12.936$ (3) Å	$\mu = 0.15$ mm^{-1}
$c = 21.510$ (6) Å	$T = 193$ (2) K
$V = 3402.1$ (16) Å^3	Prism, red
$Z = 4$	$0.40 \times 0.20 \times 0.20$ mm
$D_x = 1.331$ Mg m^{-3}	

Data collection

Syntex $P2_1$/PC diffractometer	$h = 0 \rightarrow 14$
$\theta/2\theta$ scans	$k = 0 \rightarrow 15$
3328 measured reflections	$l = 0 \rightarrow 25$
3328 independent reflections	2 standard reflections
2836 reflections with $I > 2\sigma(I)$	every 98 reflections
$\theta_{max} = 25.0°$	intensity decay: 4.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 1.2304P]$
$wR(F^2) = 0.118$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3328 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
448 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Table 1
Some short intramolecular separations (Å) in (I).

The sum of the van der Waals radii for C and H is 2.87 Å (Zefirov & Zorky, 1989).

C24···H32B	2.76	C28···H36B	2.72
C24···H32C	2.71	C28···H36C	2.77
C26···H30B	2.74	C32···H24	2.41
C26···H34B	2.82	C36···H28	2.43
C26···H35C	2.82		

Table 2
Distances (l, Å) and values for the charge density [$\rho(r)$, e Å^{-3}] and the Laplacian [$\nabla^2\rho(r)$, e Å^{-5}] at the (3,−1) critical points for attractive shortened intramolecular contacts in (I).

The sums of the van der Waals radii (Zefirov & Zorky, 1989) are N and C = 3.21 Å, N and O = 2.79 Å, N and H = 2.66 Å, and O and H = 2.45 Å.

Contact	l	$\rho(r)$	$\nabla^2\rho(r)$
N5···C8	2.813 (5)	0.092	1.19
O6···N1	2.913 (5)	0.079	0.95
N1···H16B	2.58	0.070	0.82
O1···H3	2.26	0.111	1.60
O5···H15	2.24	0.112	1.50
O7···H30B	2.34	0.095	1.28
O7···H31C	2.36	0.093	1.25
O7···H34B	2.36	0.092	1.24
O7···H35C	2.37	0.090	1.24

No Friedel pairs were measured in the data collection. All H atoms were located from difference Fourier syntheses. Methyl H atoms were allowed for as part of a rigid group, which was allowed to rotate but not tip or distort, with $U_{iso}(H) = 1.5U_{eq}(C)$. The other H atoms were allowed for using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The following distance constraints were applied: methylene C—H = 0.99 Å, methyl C—H = 0.98 Å, aromatic C—H = 0.95 Å and other C—H = 0.95 Å. The quantum-chemical calculations for (I) were performed at the B3LYP/6-31G** level using the *GAUSSIAN*98 package (Frisch *et al.*, 1998). The geometry of (I) was taken from the present X-ray data without optimization. The topological analysis of the theoretical charge-density distribution was carried out using the *EXTREME* program incorporated in the *AIMPAC* program package (Biegler-König *et al.*, 1982).

Data collection: *P3 Diffractometer Control Program* (Siemens, 1989); cell refinement: *P3 Diffractometer Control Program*; data reduction: *PROFIT* (Strel'tsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1728). Services for accessing these data are described at the back of the journal.

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