References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Cannon, J. R., Patrick, V. A., Raston, L. & White, A. H. (1978). *Aust. J. Chem.* **31**, 1265–1283.

Dannheim, J., Grahn, W., Hopf, H. & Parrodi, C. (1987). *Chem. Ber.* **120**, 871–872.

Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.

Gano, J. E., Kirschbaum, K. & Sekher, P. (1996). *Acta Cryst.* C**52**, 2334–2337.

Gano, J. E., Kluwe, C., Kirschbaum, K., Pinkerton, A. A., Sekher, P., Skrzypczak-Jankun, E., Subramaniam, G. & Lenoir, D. (1997). *Acta Cryst.* C**53**, 1723–1725.

Hopf, H. & Horn, C. (1994). *Chem. Ber.* **127**, 1781–1796.

Klein, O. (1997). Diploma thesis, Technical University of Braunschweig, Germany.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Software.* Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU4. Data Reduction Software.* Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1999). C**55**, 2080–2084

Polysulfonylamines. CXXI.† Three *N,N*-disulfonylated 1-adamantylamines

HANS-HEINRICH PRÖHL, MARTINA NÄVEKE, PETER G. JONES* AND ARMAND BLASCHETTE*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

(*Received 19 July 1999; accepted 9 September 1999*)

Abstract

N,N-Disulfonylated 1-adamantylamines, hitherto elusive, can easily be prepared by reacting 1-bromoadamantane with silver disulfonylamides suspended in anhydrous benzene. Structures have been determined for *N,N*-bis(methanesulfonyl)-1-adamantylamine, $C_{12}H_{21}NO_4S_2$, *N,N*-bis(*p*-toluenesulfonyl)-1-adamantylamine, $C_{24}H_{29}NO_4S_2$, and 2-(1-adamantyl)-1,1,3,3-tetraoxo-1,3,2-benzodithiazole [*N*-(1-adamantyl)-*o*-benzenesulfonimide], $C_{16}H_{19}NO_4S_2$. Prominent features in the molecular structures are the nearly planar central CNS_2 groupings and the exceptionally long Nsp^2—Csp^3 bonds (1.53–1.56 Å).

† Part CXX: Friedrichs & Jones (1999).

Comment

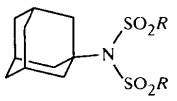
Substitution and elimination reactions of compounds containing the disulfonylamino (disulfonimide) leaving group, $-N(SO_2R)_2$, have aroused considerable attention. Thus, a simple and versatile deamination process for primary aliphatic amines involves electrophilic activation of the C(—N) atom by forming a bis(arenesulfonyl)amine, $R'N(SO_2R)_2$, followed by treatment of this derivative with nucleophiles or by subjecting it to pyrolysis (Baumgarten & Curtis, 1982, and references therein). The disulfonylamines are generally obtained in excellent yields by the reaction of one equivalent of amine with two equivalents of an arenesulfonyl chloride, either in a two-step process requiring isolation of the intermediate sulfonamide, $R'NHSO_2R$ (DeChristopher *et al.*, 1974), or more economically *via* a one-pot reaction by treating the amine with two equivalents of sulfonyl chloride and two equivalents of NaH in tetrahydrofuran (Bartsch *et al.*, 1977). However, disulfonylamines derived from such sterically hindered molecules as Ph_2CHNH_2, *exo*-2-aminonorbornane or 1-aminoadamantane could not be prepared, even though the corresponding sulfonamides are readily accessible (Hutchins *et al.*, 1978).

Following an alternative route, we have discovered that *N,N*-disulfonylated 1-adamantylamines, hitherto elusive, can be synthesized in high yields by treating 1-bromoadamantane with silver disulfonylamides, $AgN(SO_2R)_2$, suspended in benzene. It should be noted that this simple procedure is analogous to that used earlier in the synthesis of 1-adamantylsulfonates from 1-haloadamantanes and hexane suspensions of silver sulfonates (Kevill *et al.*, 1970; Takeuchi *et al.*, 1980, 1988). As the silver salts employed in the present work are to some extent soluble in benzene, the aromatic solvent was preferred to hexane [solubilities determined for $AgN(SO_2Me)_2$ in benzene: 0.4 g l^{-1} at 293 K and 0.9 g l^{-1} at 353 K]. Although acetonitrile is known to be an excellent solvent for silver disulfonylamides (Blaschette *et al.*, 1993), it could not be utilized here, as it tends to enter into pseudo-Ritter type reactions with the solutes (Pröhl *et al.*, 1997).

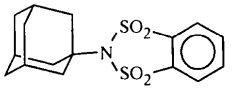
The X-ray crystal structures of three products, *N,N*-bis(methanesulfonyl)-1-adamantylamine, (I), *N,N*-bis(*p*-toluenesulfonyl)-1-adamantylamine, (II), and 2-(1-adamantyl)-1,1,3,3-tetraoxo-1,3,2-benzodithiazole, (III), authenticate them as *N,N*-disulfonylated 1-aminoadamantanes and clearly demonstrate that previous failures to isolate such compounds (Hutchins *et al.*, 1978) cannot be ascribed to an inherent steric incompatibility of a bulky adamantyl cage and two adjacent sulfonyl groups. The molecules are shown in Figs. 1–3, with selected intramolecular geometric data in Tables 1, 3 and 5. Comparable solid-state structures have been reported for seven *N*-alkyl disulfonylamines (Blaschette *et al.*, 1991; Brunzelle *et al.*, 1999; Curtis & Pavkovic, 1983; Henschel *et al.*, 1997; Jones *et al.*, 1995), includ-

© 1999 International Union of Crystallography
Printed in Great Britain – all rights reserved

ing the *N*-methyl homologues of (I) (Blaschette *et al.*, 1991) and of (II) and (III) (Jones *et al.*, 1995).



(I): $R = CH_3$
(II): $R = p\text{-}C_6H_4\text{-}CH_3$



(III)

The most prominent feature in structures (I)–(III) is provided by the exceptionally long N—C bonds (1.53–1.56 Å) at the adamantyl bridgehead C atoms, as opposed to corresponding distances of only 1.48 Å in the *N*-methyl homologues. The longest N—C bond reported previously for a similar compound (1.52 Å) was observed in *N,N*-bis(*p*-nitrobenzenesulfonyl)cyclohexylamine (Brunzelle *et al.*, 1999). Tabulation of all data available at this time suggests that the degree of N—C bond lengthening in *N*-alkyl disulfonylamines correlates with the stability order of the carbocations derived from the *N*-alkyl groups. Corroborative evidence is seen in the related trityl compound $Ph_3C^{+-}N(SO_2F)_2$, which is purely ionic in the solid state (Hiemisch *et al.*, 1996).

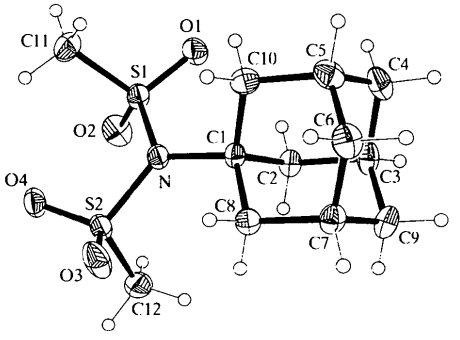


Fig. 1. The structure of compound (I) in the crystal. Ellipsoids represent 50% probability levels.

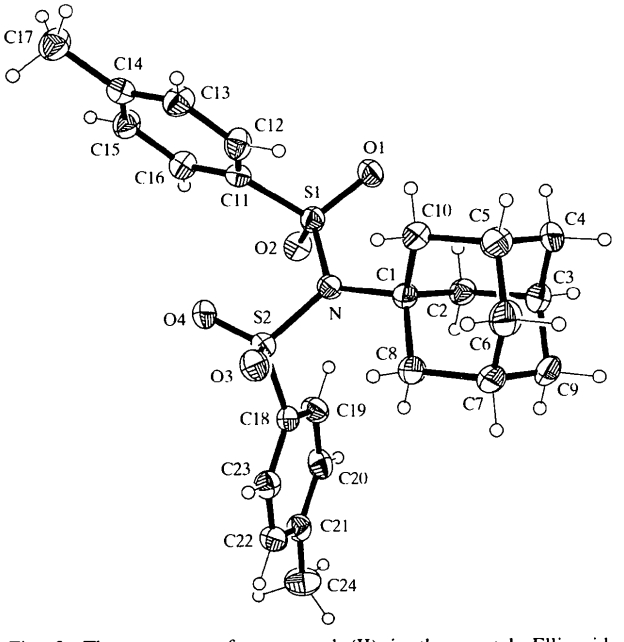


Fig. 2. The structure of compound (II) in the crystal. Ellipsoids represent 50% probability levels.

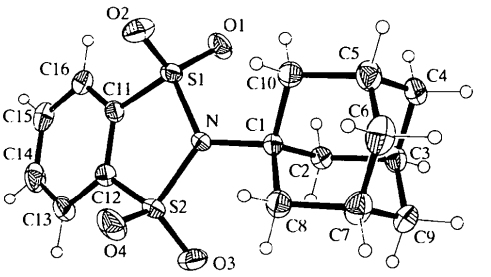


Fig. 3. The structure of compound (III) in the crystal. Ellipsoids represent 50% probability levels.

N-Organyl disulfonylamines, including (I)–(III), generally display a nearly planar central grouping formed by the N, C and two S atoms bonded to it. For (I)–(III), the N atom lies 0.115 (2), 0.002 (3) and 0.044 (2) Å out of the corresponding CS_2 plane. An atypical pyramidalization occurs with the *N*-methyl homologue of (III), where N is displaced by 0.31 Å from the CS_2 plane. The S—N—S angles in (I) and (II) are significantly smaller than in the methyl homologues, probably reflecting the steric demands of the adamantyl substituents [S—N—S 114.68 (8) and 116.09 (15)° for (I) and (II) *versus* 120.3 (1) and 123.3 (1)° for the methyl homologues]. On the other hand, the planar CNS_2 moiety of (III) exhibits a larger S—N—S angle than the pyramidal CNS_2 grouping in the corresponding *N*-methyl homologue [115.83 (10) *versus* 112.8 (1)°].

All other bond lengths and bond angles in (I)–(III) are normal when compared with a plethora of structures containing $N(SO_2R)_2$ or 1-adamantyl groups, but the torsion angles given in the tables deserve a comment.

First of all, it should be recollected that the methyl homologues of (I) and (II) contain $N(SO_2C)_2$ moieties with local pseudo C_2 symmetry, so far that stereochemically equivalent O—S—N—S and C—S—N—S torsion angles do not differ by more than 1° in the former and by more than 7° in the latter. In contrast, steric strains associated with the adamantyl groups induce more pronounced deviations from local C_2 symmetry, resulting in torsion angle differences of *ca* −16 in (I) and *ca* 50° in (II) (see O—S—N—S data in Tables 1 and 3). Molecule (III) and its methyl homologue have overall symmetries closely approximating to C_s, with the five-membered rings

forced into an envelope conformation [distance from N to the nearly planar C_6S_2 benzodithiazole fragment: 0.264 (2) Å in (III), 0.39 Å in the *N*-methyl compound].

Minor points of interest are the short intramolecular contacts H···O ≤ 2.60 Å between H atoms on the β-C atoms of the adamantyl cages and the S=O functions *syn* or *gauche* to the respective N—C bond (geometric data in Tables 2, 4 and 6, to be compared with O—S—N—C torsion angles in Tables 1, 3 and 5). Such contacts were thought at one time to play an important mechanistic role in the stereoselective pyrolytic *cis*-elimination reaction of certain *N*-alkyl disulfonylamines (Curtis *et al.*, 1981; Curtis & Pavkovic, 1983), but this was disproved by Brunzelle *et al.* (1999).

Experimental

The silver disulfonylamides used to synthesize compounds (I)–(III) were prepared and dehydrated as described elsewhere (Blaschette *et al.*, 1993). (I) and (II) are moisture-sensitive and are best handled within glove-bags or within a dry box.

Compound (I): 1-bromoadamantane (4.30 g, 20.0 mmol) was dissolved in anhydrous benzene (30 ml) and the solution added dropwise to a vigorously stirred suspension of $AgN(SO_2Me)_2$ (5.60 g, 20.0 mmol) in the same solvent (100 ml). After stirring for 96 h at room temperature in the dark, AgBr (3.75 g, 20.0 mmol) was removed by filtration, the filtrate evaporated to dryness and the crude product recrystallized from diethyl ether/petrol ether [yield 89.5% (5.50 g), m.p. 393 K].

Compound (II): the same procedure as for (I) using 1-bromoadamantane (4.30 g, 20.0 mmol) and silver bis(*p*-toluenesulfonyl)amide (8.65 g, 20.0 mmol) [yield 97% (8.9 g), m.p. 458 K].

Compound (III): the same procedure as for (I) using 1-bromoadamantane (4.30 g, 20.0 mmol) and $AgN(SO_2)_2C_6H_4$ (6.52 g, 20.0 mmol). Recrystallization was from dichloromethane/petrol ether [yield 95% (8.9 g), m.p. 523 K].

Satisfactory elemental analyses were obtained for the three substances. To produce crystals suitable for X-ray diffraction, (I) and (II) were recrystallized from diethyl ether/petrol ether, and good crystals of (III) were obtained by slow evaporation of the solvent from a diethyl ether solution in a stream of nitrogen.

Compound (I)

Crystal data

$C_{12}H_{21}NO_4S_2$
M_r = 307.42
Monoclinic
$P2_1/c$
a = 6.3450 (15) Å
b = 10.242 (3) Å
c = 21.554 (6) Å
β = 93.05 (2)°
V = 1398.7 (6) Å^3
Z = 4
D_x = 1.460 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 3.0–12.5°
μ = 0.390 mm^{-1}
T = 178 (2) K
Prism
0.75 × 0.35 × 0.30 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
3172 measured reflections
2472 independent reflections
2214 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

θ_{max} = 25°
$h = -7 \rightarrow 1$
$k = 0 \rightarrow 12$
$l = -25 \rightarrow 25$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.087
S = 1.041
2472 reflections
175 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.9426P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0140 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

N—C1	1.556 (2)	S2—N	1.6864 (15)
S1—N	1.7066 (15)		
C1—N—S1	119.76 (11)	S2—N—S1	114.68 (8)
C1—N—S2	124.10 (11)		
O1—S1—N—S2	−168.81 (9)	O1—S1—N—C1	−2.04 (15)
O2—S1—N—S2	−39.96 (11)	O2—S1—N—C1	126.81 (13)
O3—S2—N—S1	−151.13 (10)	O3—S2—N—C1	42.75 (15)
O4—S2—N—S1	−23.94 (12)	O4—S2—N—C1	169.94 (13)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O1	0.99	2.25	2.965 (2)	128
C10—H10*B*···O1	0.99	2.24	2.958 (2)	128
C8—H8*A*···O3	0.99	2.31	2.747 (2)	105

Compound (II)

Crystal data

$C_{24}H_{29}NO_4S_2$
M_r = 459.60
Orthorhombic
Pbca
a = 13.080 (3) Å
b = 11.978 (3) Å
c = 27.915 (4) Å
V = 4373.5 (16) Å^3
Z = 8
D_x = 1.396 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10.0–11.5°
μ = 0.276 mm^{-1}
T = 178 (2) K
Prism
0.70 × 0.35 × 0.20 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
3781 measured reflections
3781 independent reflections
2210 reflections with $I > 2\sigma(I)$

θ_{max} = 25°
$h = 0 \rightarrow 15$
$k = -14 \rightarrow 0$
$l = -33 \rightarrow 0$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.129$
$S = 0.944$
3781 reflections
282 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

N—C1	1.564 (4)	S2—N	1.679 (3)
S1—N	1.705 (3)		
C1—N—S1	121.3 (2)	S2—N—S1	116.09 (15)
C1—N—S2	122.6 (2)		
O1—S1—N—S2	171.69 (16)	O1—S1—N—C1	−8.5 (3)
O2—S1—N—S2	−60.4 (2)	O2—S1—N—C1	119.4 (2)
O3—S2—N—S1	−135.04 (17)	O3—S2—N—C1	45.2 (3)
O4—S2—N—S1	−6.9 (2)	O4—S2—N—C1	173.3 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O1	0.99	2.22	2.938 (4)	128
C10—H10*B*···O1	0.99	2.35	3.035 (4)	126
C8—H8*B*···O3	0.99	2.20	2.862 (4)	123

Compound (III)

Crystal data

$C_{16}H_{19}NO_4S_2$
$M_r = 353.44$
Orthorhombic
$P2_12_12_1$
$a = 7.2362$ (18) Å
$b = 7.2831$ (15) Å
$c = 29.526$ (6) Å
$V = 1556.1$ (6) Å^3
$Z = 4$
$D_x = 1.509$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 3.0$–$12.5°$
$\mu = 0.362$ mm^{-1}
$T = 178$ (2) K
Prism
0.70 × 0.30 × 0.30 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
3897 measured reflections
3572 independent reflections
3275 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 0$
$l = -38 \rightarrow 0$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.032$
3572 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.4637P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983); 1485 Friedel pairs
Flack parameter = −0.02 (7)

Table 5. *Selected geometric parameters (Å, °) for (III)*

N—C1	1.532 (2)	N—S2	1.6641 (16)
N—S1	1.6766 (17)		
C1—N—S1	121.72 (12)	S2—N—S1	115.83 (10)
C1—N—S2	122.24 (12)		
S2—N—S1—O1	−129.34 (12)	C1—N—S1—O1	45.38 (17)
S2—N—S1—O2	98.66 (12)	C1—N—S1—O2	−86.61 (17)
S1—N—S2—O3	128.93 (11)	C1—N—S2—O3	−45.76 (18)
S1—N—S2—O4	−98.94 (13)	C1—N—S2—O4	86.37 (17)

Table 6. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O1	0.99	2.60	3.272 (3)	125
C10—H10*A*···O1	0.99	2.49	3.181 (3)	127
C8—H8*A*···O3	0.99	2.46	3.154 (3)	127

Methyl-H atoms were located from difference syntheses, idealized and refined as rigid groups allowed to rotate, but not tip; other H atoms were treated as riding, starting from calculated positions.

For all compounds, data collection: *P*3 (Nicolet, 1987); cell refinement: *P*3; data reduction: *XDISK* in *P*3; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance. Mr O. Moers assisted in preparing the figures.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1364). Services for accessing these data are described at the back of the journal.

References

Bartsch, R. A., Allaway, J. R., Yandell, R. B., Lee, J. G. & McCann, D. W. (1977). *J. Chem. Eng. Data*, **22**, 453.
Baumgarten, R. J. & Curtis, V. A. (1982). *The Chemistry of Functional Groups*, Suppl. F, edited by S. Patai, pp. 929–997. Chichester: John Wiley & Sons.
Blaschette, A., Jones, P. G., Hamann, T., Näveke, M., Schomburg, D., Cammenga, H. K., Epple, M. & Steppuhn, I. (1993). *Z. Anorg. Allg. Chem.* **619**, 912–922.
Blaschette, A., Näveke, M. & Jones, P. G. (1991). *Z. Naturforsch. Teil B*, **46**, 5–14.
Brunzelle, J. S., Curtis-Palmer, V. A. & Pavkovic, S. F. (1999). *Acta Cryst.* C**55**, 624–626.
Curtis, V. A., Knutson, F. J. & Baumgarten, R. J. (1981). *Tetrahedron Lett.* **22**, 199–202.
Curtis, V. A. & Pavkovic, S. F. (1983). *Acta Cryst.* C**39**, 1077–1078.
DeChristopher, P. J., Adamek, J. P., Lyon, G. D., Klein, S. A. & Baumgarten, R. J. (1974). *J. Org. Chem.* **39**, 3525–3532.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Friedrichs, S. & Jones, P. G. (1999). *Acta Cryst.* C**55**. In the press.
Henschel, D., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 1669–1671.
Hiemisch, O., Henschel, D., Jones, P. G. & Blaschette, A. (1996). *Z. Anorg. Allg. Chem.* **622**, 829–836.
Hutchins, R. O., Kandasamy, D., Dux, F. III, Maryanoff, C. A., Rotstein, D., Goldsmith, B., Burgoyne, W., Cistone, F., Dalessandro, J. & Puglis, J. (1978). *J. Org. Chem.* **43**, 2259–2267.
Jones, P. G., Hamann, T., Schaper, W., Lange, I. & Blaschette, A. (1995). *Phosphorus Sulfur Silicon*, **106**, 91–104.

Kevill, D. N., Kolwyck, K. C. & Weitl, F. L. (1970). *J. Am. Chem. Soc.* **92**, 7300–7306.
Nicolet Instrument Corporation (1987). *P3*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
Pröhl, H.-H., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 1434–1436.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Takeuchi, K., Ikai, K., Shibata, T. & Tsugeno, A. (1988). *J. Org. Chem.* **53**, 2852–2855.
Takeuchi, K., Moriyama, T., Kinoshita, T., Tachino, H. & Okamoto, K. (1980). *Chem. Lett.* pp. 1395–1398.

Acta Cryst. (1999). C**55**, 2084–2087

An ethyl acetate inclusion complex of 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1*H*-imidazole

YOSHINOBU INOUYE,[a] SHUKO SHIMOKOSHI[a] AND YOSHIKO SAKAINO[b]

[a]*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan, and* [b]*Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Gunma 371-0044, Japan. E-mail: inouye@staff.chem.tsukuba.ac.jp*

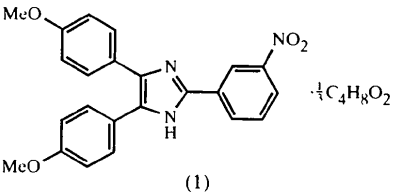
(*Received 19 July 1999; accepted 24 August 1999*)

Abstract

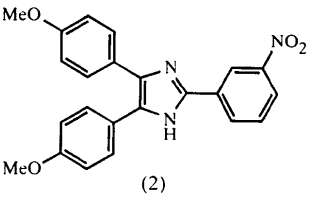
The host molecules of the yellow title compound, 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1*H*-imidazole–ethyl acetate (1/0.33), $C_{23}H_{19}N_3O_4\cdot\frac{1}{3}C_4H_8O_2$, (1), are arranged in a cross fashion through intermolecular hydrogen bonding between the N—H and N=C moieties of the imidazole ring. The ethyl acetate guest molecules are arranged in columns along the *c* axis. By heating under reduced pressure, (1) lost the guest molecules to become the non-solvated analogue, $C_{23}H_{19}N_3O_4$, without destruction of the network of host molecules.

Comment

4,5-Bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1*H*-imidazole gives four polymorphic crystals and many inclusion complexes in different colored states by changing the crystallization conditions. Several of these crystals can transform into one another by heating or by exposure to organic vapor, but the rate of transformation depends on the initial crystal form (Sakaino *et al.*, 1996). Thus, recrystallization from ethyl acetate afforded the yellow inclusion complex (1). When (1) was heated at 353 K under 2 Torr (1 Torr = 133.322 Pa), a yellow non-solvated crystal, (2), was obtained with the loss of the ethyl acetate molecules. On the other hand, either (1) or (2) when placed in contact with ethanol vapor transformed easily into red non-solvated crystals, which were identical to the crystals obtained from ethanol (Inouye & Sakaino, 1999).



(1)



(2)

The molecular structure of (1) is shown in Fig. 1. The ethyl acetate guest molecule has a linear conformation and lies along the *c* axis. Several atoms of the guest molecule show unusually short distances to those of other guest molecules at $(2-x, -y, \frac{1}{2}+z)$ and $(2-x, -y, -\frac{1}{2}+z)$. Three host molecules surround the ethyl acetate guest molecule; the shortest interatomic

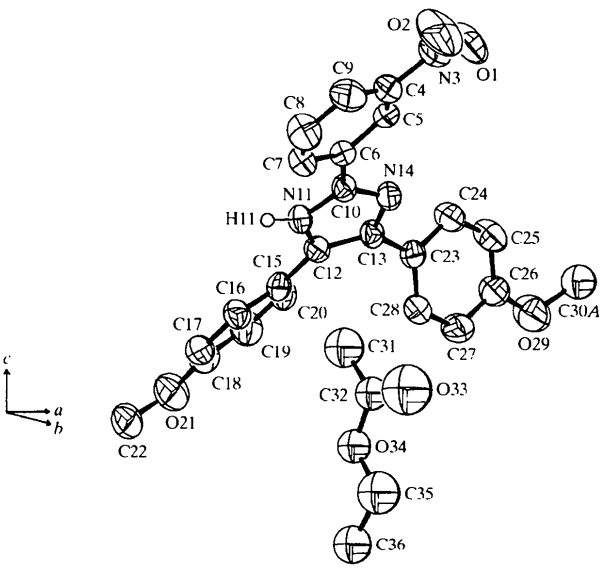


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids (*ORTEPII*; Johnson, 1976). The guest molecule is shown isotropically. For clarity, only one of the disordered positions of C30 (C30*A*) and only the H atom of the N—H group are included.

© 1999 International Union of Crystallography
Printed in Great Britain – all rights reserved