Acta Cryst. (1997). C53, 1149–1151

Exclusive Formation of Crystalline *sp*-9-(*o*-Isopropylphenyl)fluorene from its *ap* Rotamer in Solution

CAL Y. MEYERS,[a] YUQING HOU,[a] DELANO SCOTT[a] AND PAUL D. ROBINSON[b]

[a]*Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA, and* [b]*Department of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA. E-mail: robinson@geo.siu.edu*

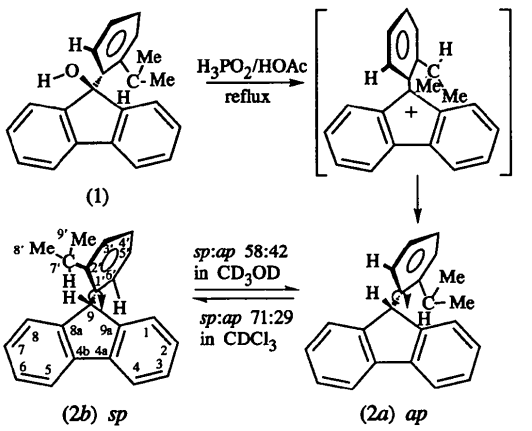
(Received 23 January 1997; accepted 6 March 1997)

Abstract

Reduction of *ap*-9-(*o*-isopropylphenyl)-9-fluorenol provided 9-(*o*-isopropylphenyl)fluorene shown to be the *sp* and *ap* rotamers in solution by ^{1}H NMR. Evaporation of the solvent yielded sharp-melting crystals identified by X-ray diffraction as *sp*-9-(*o*-isopropylphenyl)fluorene ($C_{22}H_{20}$) exclusively. A solution of these crystals redissolved in the same solvent again contained the *sp* and *ap* rotamers in the same ratio as before. The X-ray structure shows a moderately strained molecule in which the phenyl and fluorenyl rings are almost perpendicular and isopropyl–phenyl and phenyl–fluorenyl bonds are slightly distorted. While these effects do not preclude this rotamer from forming the more stable crystal lattice, they are apparently responsible for lowering its barrier of rotation sufficiently to effect the observed equilibrium in solution between it and the more strained *ap* rotamer.

Comment

Ōki and co-workers prepared 9-(*o*-isopropylphenyl)-9-fluorenol and noted it existed solely as its *ap* rotamer, (1), based on ^{1}H NMR in $CDCl_3$ (Nakamura, Nakamura & Ōki, 1977; Ōki, 1993). Our results are in agreement (Meyers *et al.*, 1997). The Ōki group also reported that reduction of (1) with HI/HOAc produces the *sp*, (2*b*), and *ap*, (2*a*), rotamers of 9-(*o*-isopropylphenyl)-fluorene in a ratio of 71:29, which they determined from ^{1}H NMR in $CDCl_3$. Although they isolated crystalline (2) from solution and reported its sharp melting point and correct elemental analysis, they did not identify the crystals as a mixture of both rotamers or one exclusively. We prepared (2) in a related manner and obtained results similar to those reported. To identify the crystals we turned to X-ray analysis (Meyers *et al.*, 1997), as we had done previously in identifying the singular crystalline rotamer that formed on evaporating a solution containing both rotameric oximes of 9-pivaloylfluorene (Robinson, Lutfi, Lim & Meyers, 1994).



The X-ray structure of crystalline (2), shown with its atom labeling in Fig. 1, identified it as the *sp* rotamer (2*b*) exclusively. The phenyl and fluorene rings are almost perpendicular, the least-squares-planes angle being 88.95 (13)°. As shown by the tabulated geometric parameters, the subsequent steric repulsion between H7′ and H9 distorts the C1′—C9 and C2′—C7′ bonds, enlarging angles C2′—C1′—C9 (*cf.* C6′—C1′—C9) and C1′—C2′—C7′ (*cf.* C3′—C2′—C7′), respectively, and atom distances C2′···C9 (*cf.* C6′···C9) and C1′···C7′ (*cf.* C3′···C7′), respectively, bringing H6′ close to the fluorene ring.

While these moderate effects of strain do not preclude the *sp* rotamer (2*b*) from forming the more stable crystal lattice, they are apparently responsible for lowering its

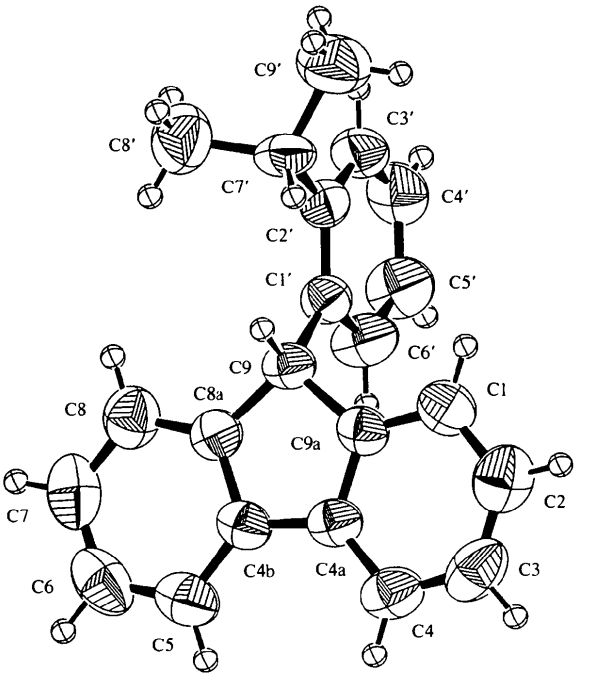


Fig. 1. The molecular structure and atom-numbering scheme of (2*b*) with displacement ellipsoids at the 50% probability level. H atoms are shown as isotropic spheres of arbitrary radii.

barrier of rotation sufficiently to effect the observed equilibrium in solution between it and the more strained *ap* rotamer (2*a*). Using theoretical parameters, Dunn & Seyler (1996) calculated K_{eq} = 2.85 (*sp*:*ap* = 74:26), which is close to the value K_{eq} = 2.44 (*sp*:*ap* = 71:29) determined by ^{1}H NMR in $CDCl_3$ by Nakamura, Nakamura & Ōki (1977) and in this study. The X-ray structure also provides a reasonable explanation for the lowered K_{eq} value we observed in methanol, 1.38 (*sp*:*ap* = 58:42). Thus, while hydrogen bonding between the methanol O atom and acidic H9 is sterically hindered in (2*b*), it is easily attained in (2*a*). The methanol···(2*a*) complex simulates (1), the increased rotational barrier resulting in the increased equilibrium proportion of the *ap* rotamer. Similarly, but to a lesser extent, a benzene π···(2*a*) complex may be responsible for the value of K_{eq} in hexane–benzene, 1.8 (*sp*:*ap* = 64:36), reported by Nakamura, Nakamura & Ōki (1977), which is intermediary between the values in chloroform and in methanol. The X-ray results verify the proximity of H6′ to the fluorene plane in accounting for its exceptionally large ^{1}H NMR shielding in (2*b*), δ 6.32 (in $CDCl_3$), compared with δ 7.57 for the same proton in the *ap* rotamer (2*a*).

Experimental

The preparation of (2*a*), (2*b*) and crystalline (2*b*) are now reported. To a stirred solution of acetic acid (10 ml) and 50% aqueous H_3PO_2 (0.5 ml, *d* = 1.274, 4.8 mmol) in a 50 ml one-necked round-bottomed flask fitted with condenser, (1) (0.10 g, 0.33 mmol) [m.p. 419–420 K (corr.); literature m.p. 420–421 K (Nakamura, Nakamura & Ōki, 1977)], was added. The colorless solution was heated to reflux and turned yellow gradually. TLC after 30 min showed the presence of (1) and another compound. After 135 min only a very small amount of (1) remained; the mixture was cooled, diluted with water and extracted several times with ether. The combined extracts were washed with aqueous $NaHCO_3$, then water, dried (anhydrous $MgSO_4$) and rotary evaporated *in vacuo* leaving a semi-solid paste, 0.094 g. TLC showed only one major spot and a trace of (1). However, ^{1}H NMR ($CDCl_3$) indicated a yield of 95% of (2) composed of its *sp*, (2*b*), and *ap*, (2*a*), rotamers in a ratio of 71:29, and 5% of starting material. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.45 (*d*, *J* = 6.9 Hz, 6H; *ap*), 1.50 (*d*, *J* = 6.9 Hz, 6H; *sp*), 1.56 (*hep*, *J* = 6.9 Hz, 1H; *ap*), 3.78 (*hep*, *J* = 6.9 Hz, 1H; *sp*), 4.95 (*s*, 1H; *ap*), 5.50 (*s*, 1H; *sp*), 6.32 (*dd*, *J* = 7.8, 1.2 Hz, 1H; *sp*), 6.88 (*ddd*, *J* = 7.8, 1.2 Hz, 1H; *sp*), 7.15–7.43 (*m*, 7H, *sp*; 11H, *ap*), 7.57 (*dd*, *J* = 7.2, 2.1 Hz, 1H; *ap*), 7.82 (*dd*, *J* = 7.5, 0.9 Hz, 2H; *sp*), 7.83 (*dd*, *J* = 7.5, 1.2 Hz, 1H; *sp*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.11, 24.41, 28.09, 29.50, 48.98, 56.42, 119.90, 120.08, 124.66, 125.04, 125.16, 125.57, 126.13, 126.88, 126.98, 127.06, 127.09, 127.23, 127.30, 127.82, 127.97, 133.00, 138.45, 140.24, 141.17, 146.80, 148.47, 148.71, 148.84. Recrystallization from hexanes–methanol provided colorless single crystals [m.p. 361.5–362.5 K (corr.); literature m.p. 361–362 K (Nakamura, Nakamura & Ōki, 1977)], which were used for the X-ray study and shown to be the *sp* rotamer exclusively. The ^{1}H NMR spectrum of a solution of these crystals redissolved in CD_3OD showed both rotamers again were present, in an *sp*:*ap* ratio of 58:42. Similar results were obtained when the reduction of (1) was carried out with H_3PO_2/I_2 catalyst.

Crystal data

$C_{22}H_{20}$
M_r = 284.40
Monoclinic
$P2_1/c$
a = 11.7734 (17) Å
b = 15.773 (2) Å
c = 8.7960 (16) Å
β = 95.182 (14)°
V = 1626.7 (4) Å^3
Z = 4
D_x = 1.161 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 22 reflections
θ = 10.3–17.3°
μ = 0.065 mm^{-1}
T = 296 K
Prism
0.33 × 0.30 × 0.29 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 4° min^{-1} in ω)
Absorption correction: none
3064 measured reflections
2864 independent reflections
1090 reflections with $I > 2\sigma(I)$

R_{int} = 0.032
θ_{max} = 25°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 10$
3 standard reflections
every 150 reflections
intensity decay: −0.56%

Refinement

Refinement on F^2
$R(F)$ = 0.046
$wR(F^2)$ = 0.109
S = 1.173
2864 reflections
201 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.3571P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.188 e Å^{-3}
$\Delta\rho_{min}$ = −0.156 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1′—C9	1.529 (4)	C6′···C9	2.492 (4)
C2′—C7′	1.524 (5)	C1′···C7′	2.554 (4)
C2′···C9	2.583 (4)	C3′···C7′	2.539 (5)
C2′—C1′—C9	124.0 (3)	C1′—C2′—C7′	122.0 (3)
C6′—C1′—C9	116.9 (3)	C3′—C2′—C7′	120.5 (3)

C—H distances for the riding H atoms ranged from 0.93 to 0.98 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN SHELXL*93 and *PLATON* (Spek, 1990).

Partial support of this research from Southern Illinois University through doctoral fellowship (YH), distinguished professorship (CYM) and NCRR Minority Initiative (DS) funding and from the University Research Foundation (URF, La Jolla, CA) is graciously acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1290). Services for accessing these data are described at the back of the journal.

References

Dunn, H. E. & Seyler, J. W. (1996). Personal communication.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Meyers, C. Y., Hou, Y., Scott, D., Robinson, P. D., Dunn, H. E. & Seyler, J. W. (1997). *Am. Chem. Soc. Natl Meet.*, April 13–17, San Francisco. Abstracts, ORGN 352.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nakamura, M., Nakamura, N. & Ōki, M. (1977). *Bull. Chem. Soc. Jpn*, **50**, 1097–1101.
Ōki, M. (1993). *The Chemistry of Rotational Isomers*, Vol. 30, *Reactivity and Structure Concepts in Organic Chemistry*. New York: Springer-Verlag.
Robinson, P. D., Lutfi, H. G., Lim, L. W. & Meyers, C. Y. (1994). *Acta Cryst.* C**50**, 1728–1732.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Acta Cryst. (1997). C**53**, 1151–1153

S-Methyl β-*N*-[4-(Dimethylamino)benzylidene]dithiocarbazate

CUN-YUAN ZHAO,[a] CHUN-YING DUAN,[a] YU-PENG TIAN,[a] XIAO-ZENG YOU[a] AND THOMAS C. W. MAK[b]

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*Department of Chemistry, The Chinese University of Hong Kong, Hong Kong. E-mail: youxz@njnet.nj.ac.cn*

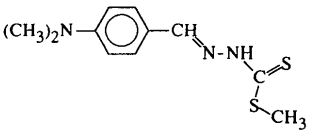
(*Received 12 December 1996; accepted 24 March 1997*)

Abstract

The title compound, $C_{11}H_{15}N_3S_2$, a Schiff base, forms a centrosymmetric dimeric structure linked by N—H···S hydrogen bonds. The dithiocarbazate moiety shows an *E* configuration about both the C2—N2 and C1—N1 bonds.

Comment

Recently, there has been considerable interest in the chemistry of Schiff base compounds containing N and S donors and their metal complexes. This is due to their biological properties, chelating ability with transition metal ions (Ali & Tarafdar, 1977; Ali & Bose, 1984; Davies, El-Sayed, El-Toukhy & Henary, 1990; Tian, Duan, Lu, You, Fun & Kandasamy, 1996) and non-linear optical properties (Tian, Duan, Lu, You & Mak, 1996). As part of our studies on the synthesis and characterization, as well as the potential non-linear optical properties, of new Schiff base derivatives, we report here the crystal structure of the title compound, (1).



(1)

The dithiocarbazate moiety shows an *E* configuration about both the C2—N2 and C1—N1 bonds as found in most dithiocarbazates (Fun *et al.*, 1995) and thiosemicarbazones (Mathew & Palenik, 1971). Though non-planar as a whole, the molecule contains two planar fragments, namely the dithiocarbazate moiety, (I), and the aminophenyl moiety, (II). The dihedral angle between them is *ca* 7.2° [mean deviations of (I) and (II) are 0.007 and 0.011 Å, respectively]. The value for the C1—S1 bond, 1.663 Å, agrees well with those of related compounds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond (Sutton, 1965). The corresponding bond distance for C1—N1, 1.333 Å, is indicative of some double-bond character.

The H atom attached to the amino N atom has the potential to act as a hydrogen-bond donor. The intermolecular hydrogen bonds which link molecules to-

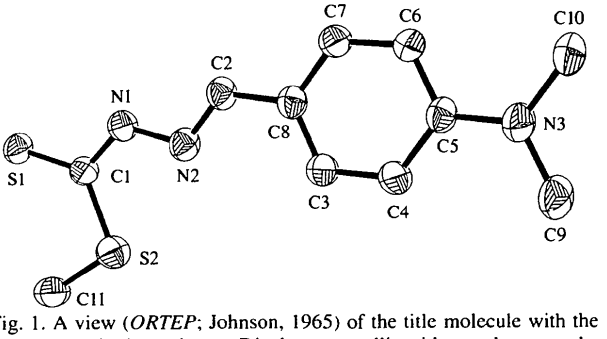


Fig. 1. A view (*ORTEP*; Johnson, 1965) of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.