Sterically Congested Molecules. Part 2.[1] Structure of *N*-(2,2,5,5-Tetramethylcyclopentylidene)-4-amino-3,5-dimethylphenol: Accommodation of Front Strain along the C=N Double Bond

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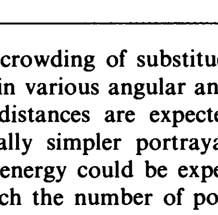
A crystal of the title compound was found to be composed of two kinds of independent molecules, **1** and **1′**, which are interconnected by a rare type OH ··· OH ··· N of hydrogen bonding. Despite their different role in such hydrogen bonding, both molecules have similar structural properties. Front strain along the C=N double bonds, as characterized by intramolecular non-bonding distances, appears to be accommodated by moderate widening of mainly the C=N–C angles together with a somewhat smaller opening of the C–C=N angles but little deformation of the aromatic ring.

Steric crowding of substituents at a C=N double bond may result in various angular and torsional deformations, whereas bond distances are expected to change much less. A geometrically simpler portrayal of the internal distribution of strain energy could be expected for a molecular architecture in which the number of possible deformations is reduced by incorporation of a less flexible ring system.

We have analysed the crystal structure of the title compound **1**, carrying opposing methyl groups at both ends of its C=N double bond, to obtain a comparison of its geometrical deformations with the distances of repulsive intramolecular contacts. In particular, the C=N–C angle could have been expected to behave as a rather soft region for the accommodation of strain. As the basicities of imines are not well known, we were also interested in testing the accessibility of the imino group of **1** for hydrogen bonding with the phenolic hydroxy function of a neighbouring molecule.



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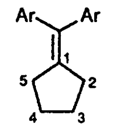

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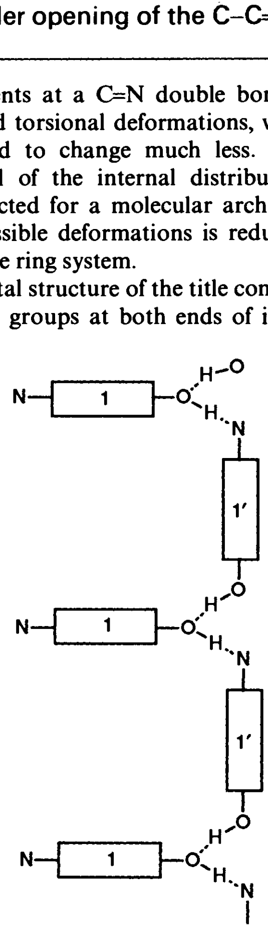


Scheme 1

Results and Discussion

Fig. 1 displays the solid-state structure of the imine **1** as an ORTEP plot based on the atomic co-ordinates in Table 1. The repeating unit consists of two independent molecules (**1** and **1′**) which play different roles in hydrogen bonding: molecule **1** uses only its phenolic function, whereas molecule **1′** contributes to hydrogen bonding with both its imino and hydroxy functions. The O(1) atom of molecule **1** engaged in bonding to the nitrogen atom N(1′) of molecule **1′** is additionally used as a hydrogen-bond base towards the phenolic function of a different molecule (**1′**) which is situated at the next position down the stack of **1′** molecules. This connectivity, shown in Scheme 1, thus avoids formation of the repeating OH ··· N arrangement which had been found for *N*-(isopropylidene)-4-aminophenol[2] and which would probably not allow for a sufficiently close spatial packing due to the bulky substituents in the case of **1**. The triply coordinated nitrogen atom N(1′) lies almost exactly in the plane spanned by C(1′), C(10′), and O(1), with the H(1) atom connecting O(1) and N(1′) slightly off this plane.

Most of the geometrical parameters are seen to be quite similar for molecules **1** and **1′** from the collections in Tables 2–5. For the recognition of possible artifacts, some structural features of the cyclopentylidene rings may be compared with those of models from the literature. The peculiar C(3)–C(4) bond contraction must be partially due to disorder but is also found in **2** (1.48 Å) with Ar = 4-acetoxyphenyl.[3] Compression of the four intraannular angles other than C(2)–C(1)–C(5) is a common property of cyclopentanone[4] and some of its derivatives.[5,6] Tables 2–5 show also the merits and weaknesses of one of the widely-used force-field models, MM2 in the MMX87 version,[7] which was applied in an energy minimization of the **1**/**1′** hydrogen-bonded pair. Whereas the hydrogen bond and most of the bond angle trends are reasonably reproduced by the MMX program, its performance in the calculation of bond lengths appears to be rather poor, especially for the imino function. The necessity for a special parametrization of cyclopentane fragments has recently been acknowledged in the MM3 version.[8]

The N–C(1) and N–C(10) bond lengths (Table 2) in **1** and **1′** are close to their normal values of 1.24–1.28 and 1.40–1.46 Å, respectively. C(1) is perfectly planar in both molecules, and the C=N double bonds are at most only slightly twisted (*ca.* 3°) from planarity. This may be a consequence of torsional twist in the cyclopentylidene rings about the C=N double-bond axes, causing C(7,7′) and C(8,8′) to occupy pseudo-axial positions whereas the pseudo-equatorial C(6,6′) and C(9,9′) atoms require more space by protruding further into the double-bond regions. Table 5 shows that the C(9) and C(9′) atoms have the shortest distances from the opposing aromatic *ipso*-carbon atoms C(10) and C(10′), respectively, but even these distances are much longer (by at least 0.3 Å) than those in **3**[9] and can thus be considered as only moderately repulsive. The corresponding closest carbon contact to phenyl in the recently

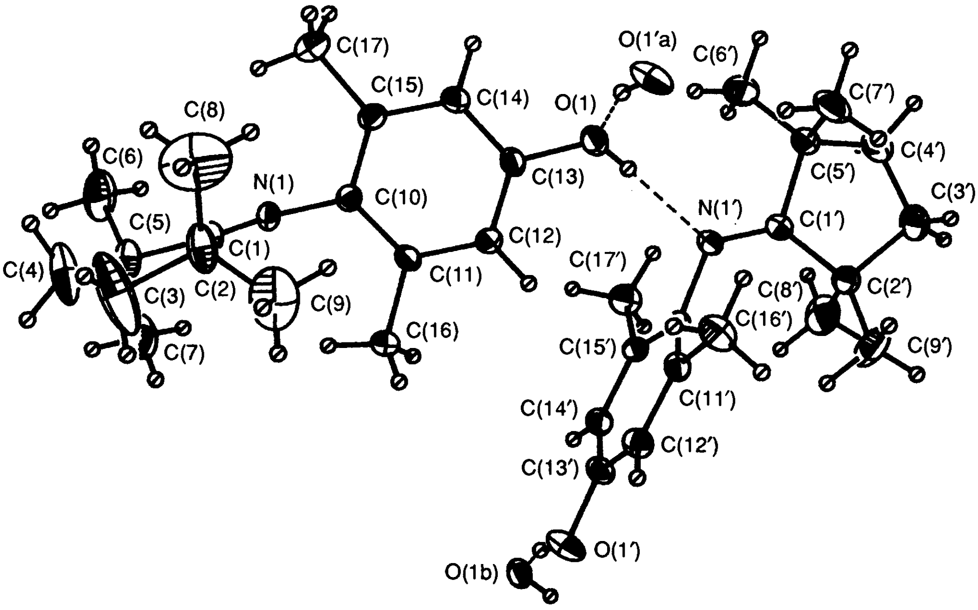


Fig. 1 Structure and crystallographic numbering of imine **1**, with thermal ellipsoids at the 20% probability level

Table 1 Final atomic co-ordinates for **1** at room temperature

Atom	*x*	*y*	*z*
O(1)	0.1189(2)	0.2235(4)	0.1252(2)
N(1)	0.2399(2)	0.4905(5)	−0.0713(2)
C(1)	0.2989(3)	0.5017(7)	−0.0617(3)
C(2)	0.3571(3)	0.4430(10)	0.0026(4)
C(3)	0.4106(3)	0.5252(12)	−0.0157(5)
C(4)	0.3934(3)	0.5616(10)	−0.0964(4)
C(5)	0.3215(3)	0.5887(8)	−0.1217(4)
C(6)	0.2897(3)	0.5263(8)	−0.2006(3)
C(7)	0.3069(3)	0.7643(7)	−0.1185(3)
C(8)	0.3643(3)	0.2679(9)	−0.0034(4)
C(9)	0.3574(3)	0.4797(10)	0.0819(3)
C(10)	0.2122(2)	0.4201(6)	−0.0185(3)
C(11)	0.1963(2)	0.5169(6)	0.0340(3)
C(12)	0.1660(2)	0.4531(6)	0.0829(3)
C(13)	0.1491(2)	0.2931(7)	0.0775(3)
C(14)	0.1631(2)	0.1968(6)	0.0245(3)
C(15)	0.1940(2)	0.2587(7)	−0.0251(3)
C(16)	0.2117(2)	0.6951(6)	0.0388(3)
C(17)	0.2038(3)	0.1525(6)	−0.0870(3)
O(1′)	0.1866(2)	0.9924(4)	0.2314(2)
N(1′)	0.0476(2)	0.4529(5)	0.1908(2)
C(1′)	0.0003(2)	0.3937(6)	0.2144(3)
C(2′)	−0.0315(3)	0.4890(7)	0.2642(3)
C(3′)	−0.0791(3)	0.3685(7)	0.2791(4)
C(4′)	−0.0963(3)	0.2543(7)	0.2131(3)
C(5′)	−0.0339(3)	0.2331(7)	0.1935(3)
C(6′)	−0.0459(2)	0.1895(7)	0.1100(3)
C(7′)	0.0075(3)	0.1049(6)	0.2452(3)
C(8′)	−0.0698(3)	0.6291(7)	0.2190(3)
C(9′)	0.0132(3)	0.5517(8)	0.3373(3)
C(10′)	0.0806(2)	0.5767(6)	0.2043(3)
C(11′)	0.1381(3)	0.5899(6)	0.2623(3)
C(12′)	0.1727(2)	0.7296(7)	0.2695(3)
C(13′)	0.1515(3)	0.8544(7)	0.2193(4)
C(14′)	0.0963(3)	0.8361(3)	0.1585(3)
C(15′)	0.0608(2)	0.6971(6)	0.1495(3)
C(16′)	0.1656(2)	0.4523(6)	0.3165(3)
C(17′)	0.0043(2)	0.6741(6)	0.0781(3)

Table 2 Experimental bond lengths/Å for the two molecules **1** and **1′**, and calculated values from the force-field model (MMX87)

	X-Ray		Calculated	
Bond	**1**	**1′**	**1**	**1′**
N(1)–C(1)	1.254(7)	1.268(7)	1.29	1.29
N(1)–C(10)	1.418(7)	1.435(6)	1.48	1.48
C(1)–C(2)	1.529(7)	1.531(9)	1.52	1.52
C(1)–C(5)	1.522(9)	1.528(7)	1.52	1.52
C(2)–C(3)	1.482(11)	1.532(9)	1.55	1.55
C(2)–C(8)	1.479(11)	1.528(8)	1.54	1.54
C(2)–C(9)	1.486(10)	1.496(7)	1.54	1.54
C(3)–C(4)	1.445(11)	1.498(9)	1.53	1.53
C(4)–C(5)	1.516(9)	1.525(9)	1.54	1.54
C(5)–C(6)	1.497(8)	1.518(8)	1.54	1.54
C(5)–C(7)	1.507(9)	1.532(7)	1.54	1.54
C(10)–C(11)	1.382(8)	1.385(6)	1.41	1.41
C(10)–C(15)	1.401(8)	1.395(7)	1.41	1.41
C(11)–C(12)	1.378(8)	1.375(8)	1.40	1.40
C(11)–C(16)	1.523(7)	1.520(7)	1.51	1.51
C(12)–C(13)	1.382(7)	1.374(8)	1.40	1.40
C(13)–C(14)	1.367(8)	1.381(7)	1.40	1.40
C(14)–C(15)	1.390(8)	1.380(7)	1.40	1.40
C(15)–C(17)	1.506(8)	1.515(6)	1.51	1.51
O(1)–C(13)	1.377(7)	1.366(7)	1.36	1.36
O(1)–H(1)	0.760(7)	0.855(7)		

studied pinacolone anil fragment **4**[10] is also comparable (3.41 Å). When hydrogen atoms are included at C(9) in **1**/**1′**, their shortest distance from the aromatic *ipso*-carbon atoms (C10) is *ca.* 2.65 Å, matching values from cyclophane derivatives[11] and from an imine[12] which could have avoided such an interaction (2.68 Å) if strain had become prohibitive.

The aromatic rings are in an almost orthogonal conformation (Table 4) with respect to the C=N double bonds, maximizing conjugative interaction of the lone electron-pair with the aromatic π system. Their *ipso*-carbon atoms C(10) and C(10′) appear to be slightly pyramidal in a sense which moves the *ortho*-methyl groups C(16, 17) away from C(8) and C(9). Of the two kinds of sp^2-centred angles which control this repulsion, C(1)–N(1)–C(10) is somewhat less opened than N(1)–C(1)–C(2). It thus appears that the lone electron-pair is not a soft abutment against steric repulsion. The C(1)–N(1)–C(10) angle, for which the value of 119° in **5**[13] may be taken as an almost strain free reference, is a little larger for molecule **1** than at the hydrogen-bonded N(1′) in molecule **1′**. Although the difference of such angles might be statistically insignificant, it is re-

Table 3 Experimental[a] angles/° for the two molecules **1** and **1′**, and calculated values from the force-field model (MMX87)

	X-Ray		Calculated	
Angle	**1**	**1′**	**1**	**1′**
C(1)–N(1)–C(10)	124.9(4)	123.2(5)	127.3	125.7
O(1)–N(1′)–C(1′)		129.6(6)		127.2
O(1)–N(1′)–C(10′)		106.6(6)		107.0
N(1)–C(1)–C(2)	131.7(6)	131.5(5)	129.0	128.6
N(1)–C(1)–C(5)	118.9(4)	119.3(5)	118.7	119.5
C(2)–C(1)–C(5)	109.5(5)	109.2(5)	112.3	112.0
C(1)–C(2)–C(3)	101.9(6)	102.9(5)	101.8	101.6
C(1)–C(2)–C(8)	110.0(5)	110.4(5)	110.9	110.9
C(3)–C(2)–C(8)	109.4(7)	108.1(5)	110.2	110.3
C(1)–C(2)–C(9)	116.4(6)	115.2(5)	114.6	115.4
C(3)–C(2)–C(9)	111.0(6)	111.3(5)	109.2	108.7
C(8)–C(2)–C(9)	108.0(6)	108.6(5)	109.8	109.6
C(2)–C(3)–C(4)	110.7(5)	106.9(6)	105.3	105.2
C(3)–C(4)–C(5)	105.5(6)	104.0(4)	104.4	104.5
C(1)–C(5)–C(4)	104.1(5)	104.1(5)	102.3	103.2
C(1)–C(5)–C(6)	112.1(5)	112.7(5)	113.1	112.0
C(4)–C(5)–C(6)	112.2(6)	112.0(4)	110.7	110.2
C(1)–C(5)–C(7)	108.5(6)	107.8(4)	109.4	109.5
C(4)–C(5)–C(7)	110.3(5)	109.8(5)	111.5	111.2
C(6)–C(5)–C(7)	109.6(5)	110.2(5)	110.3	110.6
N(1)–C(10)–C(11)	119.0(5)	119.6(4)	119.8	119.7
N(1)–C(10)–C(15)	120.6(5)	118.7(4)	120.2	119.8
C(11)–C(10)–C(15)	119.9(5)	120.5(5)	119.9	120.3
C(10)–C(11)–C(12)	120.2(5)	119.1(5)	119.3	119.3
C(10)–C(11)–C(16)	121.0(5)	121.9(5)	122.5	121.7
C(12)–C(11)–C(16)	118.9(5)	118.9(4)	118.2	119.0
C(11)–C(12)–C(13)	119.9(5)	121.1(4)	121.4	120.7
O(1)–C(13)–C(12)	122.1(5)	118.2(4)	120.7	120.2
O(1)–C(13)–C(14)	117.4(5)	122.4(5)	120.5	120.2
C(12)–C(13)–C(14)	120.6(5)	119.4(5)	118.8	119.6
C(13)–C(14)–C(15)	120.5(5)	120.8(5)	121.0	120.7
C(10)–C(15)–C(14)	118.9(5)	118.7(4)	119.5	119.3
C(10)–C(15)–C(17)	122.0(5)	121.7(4)	121.8	121.8
C(14)–C(15)–C(17)	119.0(5)	119.5(4)	118.6	118.7
O(1)–H(1)–N(1′)	174.6(8)			
O(1)–H(1′a)–O(1′a)[a]	160.3(8)			

[a] Symmetry transformation: $x, -1 + y, z$.

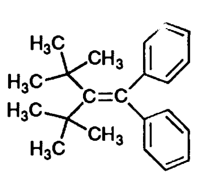
Table 4 Torsional angles/° for the two molecules **1** and **1′**, and calculated values from the force-field model (MMX87)

	X-Ray		Calculated	
Angle	**1**	**1′**	**1**	**1′**
C(1)–N(1)–C(10)–C(11)	93.9(6)	100.4(6)	92.6	93.9
C(1)–N(1)–C(10)–C(15)	−93.8(6)	−92.4(7)	−91.1	−90.4
C(2)–C(1)–N(1)–C(10)	2.8(10)	−4.2(8)	−0.3	−0.4
C(5)–C(1)–N(1)–C(10)	−176.7(5)	176.7(4)	179.5	178.9
N(1)–C(10)–C(11)–C(12)	176.2(4)	173.1(5)	179.9	179.3
N(1)–C(10)–C(11)–C(16)	−3.6(6)	−4.6(9)	+0.7	+2.2
N(1)–C(10)–C(15)–C(14)	−175.7(4)	−173.5(5)	−179.5	−179.5
N(1)–C(10)–C(15)–C(17)	1.0(6)	2.1(9)	−2.3	−3.5
C(13)–C(14)–C(15)–C(17)	−175.0(4)	−173.9(6)	−176.0	−174.7
C(13)–C(12)–C(11)–C(16)	177.3(4)	176.6(6)	177.1	176.2

Table 5 Experimental[a] non-bonded distances/Å for the two molecules **1** and **1′**, compared with force-field calculations (MMX87)

	X-Ray		Calculated	
Contact	**1**	**1′**	**1**	**1′**
C(8)–C(10)	3.50	3.41	3.52	3.54
C(8)–C(15)	3.63	3.52	3.62	3.62
C(8)–C(17)	3.51	3.47	3.53	3.53
C(9)–C(10)	3.19	3.22	3.23	3.16
C(9)–C(11)	3.38	3.43	3.37	3.31
C(9)–C(16)	3.54	3.57	3.48	3.53
O(1)–C(6′)	3.55		3.54	
O(1)–C(7′)	3.88		3.71	
O(1)–C(1′)	3.75		3.71	
O(1)–O(1′a)[a]	2.82			
O(1)–N(1′)	2.81		2.78	
O(1)–H(1′)[a]	2.00			
N(1′)–H(1)	2.05			

[a] Symmetry transformations: $x, -1 + y, z$.



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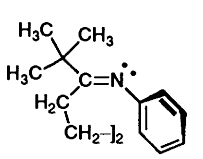

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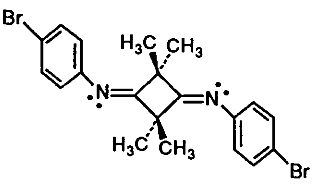

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produced by the force-field calculation in Table 3. Hydrogen-bonding has therefore little structural consequence at the accepting nitrogen atom.

Conclusion

The details reported demonstrate that 'solvation' at the imino nitrogen atom of **1′** is not impeded by the bulky substituents; indeed, our force-field calculation on the **1**/**1′** aggregate converged without problems. The C=N–C angle responds to repulsive strain by a moderate opening (*ca.* 5°). Since **1** has little skeletal flexibility, the orthogonal aryl conformation with respect to the C=N double bond is certainly maintained in solution for **1** as well as its parent imine without the hydroxy function. The lone electron pair at nitrogen will therefore act as a π-donor substituent in this conformation, allowing for electronically facilitated (*Z*/*E*)-diastereotopomerization and electrophilic aromatic substitution of such compounds.[14]

For a clear demonstration of response to front strain, imine **1** appears to be a better model than the imines[15–18] of di-*tert*-butyl ketone which have more internal degrees of freedom and tend to disordering of the *tert*-butyl groups.[15–17] However, the ideal model should possess a buttressing 2,2,5,5-tetraalkyl portion without the distinct twisting observed in **1**.

Experimental

N-(*2,2,5,5-Tetramethylcyclopentylidene*)-*4-amino-3,5-dimethylphenol* **1**.—Colourless, rod-shaped crystals were selected from the product of a multistep synthesis:[14] m.p. 167–169 °C (cyclohexane).

X-Ray Structural Analysis and Refinement.—4298 reflections were collected at 22 °C, and three reflections monitored for intensity and orientation control, using ω-scans with 0.80° + 0.35 tan θ, $t_{max} = 120$ s. Of the 3213 unique and observed reflections, 2278 with $I > 2\sigma(I)$ were used for least-squares refinements with 343 parameters, leading to $R = 0.0647$, $R_w = 0.0484$, $w^{-1} = \sigma^2(F_o)$, final residual electron densities between

$+0.27$ and -0.24 e Å^{-3}. The structure was solved by SHELXS-86[19] and refined by SHELXTL-Plus.[20] All hydrogen atoms were used at calculated positions except for those at oxygens O(1) and O(1′). The latter, H(1a) and H(1b), were found in the difference Fourier map and then also refined in the riding mode.

Crystal Data.—$C_{17}H_{25}NO$, $M = 259.4$, monoclinic, $P2_1/n$ (no. 14), $a = 21.901(5)$, $b = 8.354(2)$, $c = 18.364(5)$ Å, $\beta = 107.76(2)°$, $V = 3.200(1)$ nm^3, $Z = 8$, $D_x = 1.074$ g cm^{-3}, crystal size/mm = $0.1 \times 0.4 \times 0.5$, $F(000) = 1136.0$, μ(Mo-Kα) = 0.613 cm^{-1}, $\lambda = 0.710\,69$ Å. Lists of thermal parameters and hydrogen atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

References

1 Part 1, R. Knorr, E. Lattke and E. Räpple, *Liebigs Ann. Chem.*, 1980, 1207.

2 D. R. Holmes and H. M. Powell, *Acta Crystallogr.*, 1953, **6**, 256.

3 G. Precigoux, B. Busetta, C. Courseille and M. Hospital, *Acta Crystallogr., Sect. B*, 1978, **34**, 3300.

4 H. Kim and W. D. Gwinn, *J. Chem. Phys.*, 1969, **51**, 1815.

5 F. E. Elfehail, W. W. Zaiac, J. P. Hazel and G. T. DeTitta, *Acta Crystallogr., Sect. B*, 1977, **33**, 1962.

6 R. Kivekäs and T. Simonen, *Acta Chem. Scand., Ser. B*, 1979, **33**, 627.

7 MM2: N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127; N. L. Allinger and Y. H. Yuh, *Pure Appl. Chem.*, 1983, **55**, 191; distributed as PC-MODEL-PI by Serena Software, Bloomington, Indiana, USA.

8 N. L. Allinger, Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8551; N. L. Allinger, H. J. Geise, W. Pyckhout, L. A. Paquette and J. C. Gallucci, *J. Am. Chem. Soc.*, 1989, **111**, 1106.

9 A. Mugnoli and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1831.

10 R. Knorr, H. Dietrich and W. Mahdi, *Chem. Ber.*, 1991, **124**, issue 8.

11 P. N. Swepston, S.-T. Lin, A. Hawkins, S. Humphrey, S. Siegel and A. W. Cordes, *J. Org. Chem.*, 1981, **46**, 3754.

12 T. A. Hamor, W. B. Jennings, L. D. Proctor, M. S. Tolley, D. R. Boyd and T. Mullan, *J. Chem. Soc., Perkin Trans. 2*, 1990, 25.

13 P. Stadel, W. Jensen, J. Worman and R. A. Jacobson, *J. Chem. Soc., Perkin Trans. 2*, 1976, 536. Note that it is difficult to retrieve the full structure because of some misprinting in the published co-ordinates.

14 J. Mehlstäubl, Doctoral Dissertation, University of Munich, 1985.

15 B. Hall, J. B. Farmer, H. M. M. Shearer, J. D. Sowerby and K. D. Wade, *J. Chem. Soc., Dalton Trans.*, 1979, 102.

16 W. Clegg, R. Snaith, H. M. M. Shearer, K. Wade and G. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1983, 1309.

17 E. Niecke, M. Nieger, C. Gärtner-Winkhaus and B. Kramer, *Chem. Ber.*, 1990, **123**, 477.

18 D. Barr, R. Snaith, R. E. Mulvey and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1987, 2141.

19 G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, Univ. of Göttingen, Germany, 1986.

20 G. M. Sheldrick, SHELXTL-Plus, Nicolet XRD, Madison, Wisconsin, USA, 1987.

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