X-Ray Structure and Force Field Calculations of a Chiral Benzaldehyde Schiff Base

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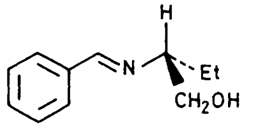
The crystal structure of the Schiff base formed from benzaldehyde and (*R*)-2-aminobutan-1-ol is compared to one obtained from force-field calculations employing a new parameter set; the probable structure of the hydrogen-bonded Schiff base dimer is discussed.

With its various parameter sets adapted to different needs, molecular mechanics has become a viable alternative to quantum mechanics for the description of large molecules.[1] In contrast to the sophisticated force-fields developed for the peptide C–N single bond[2] little has been done about the C=N double bond, despite the importance of imines in biochemistry. In this communication, we describe the structure of a simple chiral imine based on *X*-ray data and force-field calculations using a newly developed set of parameters. Also, we present the calculated structure of the hydrogen-bridged imine dimer.

The Schiff base (**1**) was obtained by treating benzaldehyde with an equimolar amount of (*R*)-2-aminobutan-1-ol in diethyl ether over molecular sieve. Slow crystallization from hexane yielded white needles on which a single-crystal *X*-ray diffraction analysis was carried out.† In the lattice, the molecules of (**1**) are connected *via* hydrogen bonds between the OH groups into infinite helical chains. The structure of one of the molecules is shown in Figure 1.



(**1**)

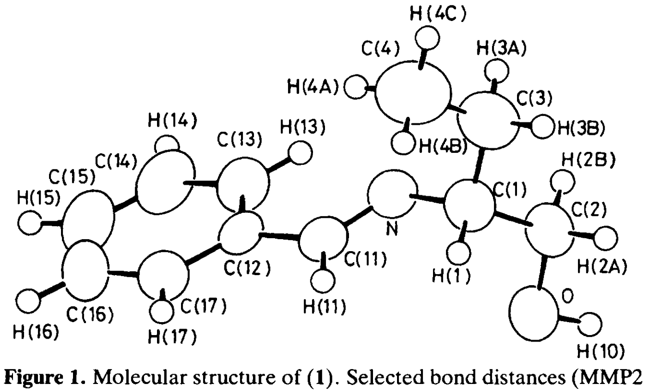


Figure 1. Molecular structure of (**1**). Selected bond distances (MMP2 calculated values in parentheses): C(2)–C(1) 1.514 (1.535), C(1)–N 1.472 (1.473), N–C(11) 1.262 (1.284), C(11)–C(12) 1.478 Å (1.465 Å); bond angles: C(1)–N–C(11) 118.2 (120.3), N–C(11)–H(11) 118.0 (121.3), N–C(11)–C(12) 123.4 (121.1), H(11)–C(11)–C(12) 118.6° (117.6°); dihedral angles: H(1)–C(1)–N–C(11) 5.7 (−2.1), C(1)–N–C(11)–H(11) 0.8 (0.6), C(1)–N–C(11)–C(12) 180.0 (−179.8), N–C(11)–C(12)–C(17) −171.4° (−179.4°).

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† *Crystal data:* hexagonal, space group $P3_1$, $a = b = 12.555$, $c = 6.0332$ Å, $U = 823$ Å^3, $D_c = 1.43$ g cm^{-3}, $M = 177.25$, $Z = 4$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, crystal size 0.32 × 0.50 × 0.47 mm. Of a total of 4793 reflections 1740 independent reflections were observed. The final residual was $R = 0.072$ and $R_w = 0.057$ for 117 parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

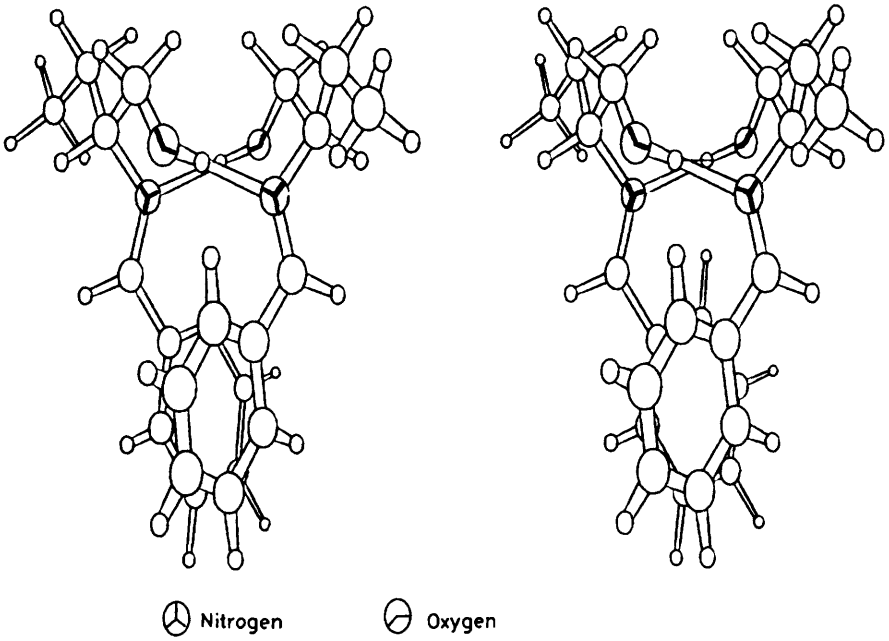

Figure 2. Stereoview of the calculated structure of the hydrogen-bridged dimer of (**1**).

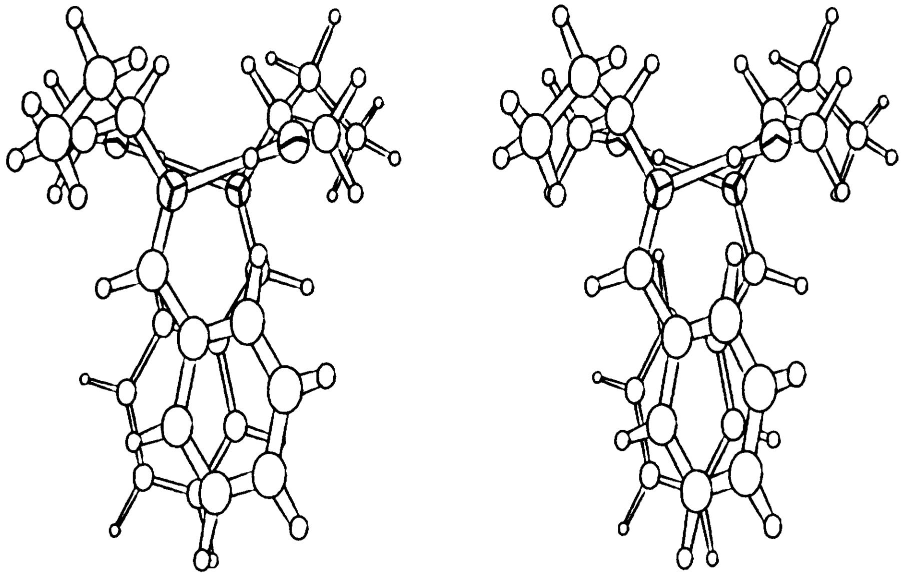

Figure 3. Stereoview of the less stable dimer of (**1**). In this case, H-eclipsing cannot be achieved, leading to a higher energy configuration compared to the one shown in Figure 2.

The benzene ring and the conjugated C=N double bond form an extended almost planar π-system. The conformation at the saturated carbon next to nitrogen corresponds to what is generally termed eclipsed with respect to the π-system.[3] This is also the assumed ground state conformation of the unsubstituted parent compound, *N*-methylenemethanamine.[4] Of the three substituents at this centre the smallest, *viz* hydrogen, eclipses the C=N bond, while the two carbon-containing groups extend out of the molecular plane. This particular conformation of azomethines has been proposed earlier on the basis of n.m.r.[5] and c.d. work.[6] Likewise the dynamic behaviour of chiral all-*trans*-retinal Schiff bases was rationalized by us on the basis of this preferred H-eclipsing.[7]

Our interest in these systems stems from the observation[8] that Schiff bases with a hydroxy group at the C_β-position, such as (**1**), show a strong tendency towards dimerization, the dimers formed exhibiting rather unusual spectral properties. In order to calculate the geometries of these aggregates, we have developed for the MMP2 force-field‡ a set of parameters for the C=N bond using structural information available for

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‡ MMP2 is Allinger's MM2 force field with the inclusion of π-electrons.

small imine derivatives.§ Calculated bond distances and angles for (**1**) are compared to experimental data in the caption of Figure 1. The agreement is generally good, especially with respect to dihedral angles which determine the three-dimensional structure of a molecule more than bond distances or even bond angles.

In the calculated dimer structure (Figure 2), the two Schiff base units are joined in a cyclic structure *via* two hydrogen bonds, the azomethine nitrogens functioning as hydrogen acceptors. From the 10-membered puckered ring thus formed the two benzene chromophores extend out on the same side, leading to the experimentally observed strong electronic interaction in this type of aggregate.[8] On account of the chiral centres, the ring conformation shown is preferred over the inverted one (Figure 3), in which the relative orientation of the two benzene rings is enantiomeric, with a calculated energy difference of 37 kJ mol^{-1}. Analysis of the c.d. spectrum of the aggregate (**1**) with its intense split Cotton effect ($\Delta\varepsilon_{257}$ −20, $\Delta\varepsilon_{215}$ 20.5) points to the exclusive formation of the more stable diastereoisomer shown in Figure 2. The H-eclipsed conformation found in the monomer is preserved in the dimer; however, the benzene rings are twisted out of the plane of the respective C=N bond, probably because of steric interaction of the *ortho*-hydrogens with the hydrogen bridges. For the enthalpy of dimerization we calculate a value of 37 kJ mol^{-1} which compares well with the experimental value (43 kJ mol^{-1}) considering the neglect of solvent effects.

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§ Experimental and *ab initio* data for methanimine (R. Pearson, Jr., and J. F. Lovas, *J. Chem. Phys.*, 1977, **66**, 4149; J. M. Lehn and B. Munsch, *Theoret. Chim. Acta*, 1970, **16**, 351), ethanimine (R. A. Eades, D. A. Weil, M. R. Ellenberger, W. E. Farneth, D. A. Dixon, and C. H. Douglass, Jr., *J. Amer. Chem. Soc.*, 1981, **103**, 5372), *N*-methylethanimine (J. Meier, A. Bauer, and H. H. Guenthard, *J. Chem. Phys.*, 1972, **57**, 1219), and propenimine (V. Bonacic-Koutecky and M. Persico, *J. Chem. Soc.*, 1983, **105**, 3388) were used to obtain stretching, bending, and torsional parameters. Details will be given in a forthcoming publication.

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