A Crystal Modification of Dibenzo[b,i][1,4,8,11]tetraaza[14]annulene: X-Ray Molecular Structure and Proton Tautomerism of the Highly π-Conjugated Form

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The crystal structure for one of crystal modifications of the title compound (taa) has been determined by X-ray diffraction at room temperature. The crystal system is monoclinic with a space group of $P2_1/a$: $a = 14.926(2)$, $b = 5.2342(8)$, $c = 19.570(2)$ Å, $\beta = 112.195(7)°$, $Z = 4$. The final R factor is 0.033 for 1443 observed reflections to 270 variables. The crystals recrystallized from xylene have been proven to be a different crystal modification from those obtained by vacuum sublimation at 250 °C. In the present crystal, two independent molecules are located on the crystallographic centres of symmetry. Each of them shows positional disorder at the amino hydrogen atoms. This modification does not exhibit the alternation of the bond lengths in the 1,3-propanediiminato linkage beyond the limit of $\Delta l < 3\sigma(l)$, which is the case for a previously reported crystal modification. These findings lend support to dynamic imine–enamine tautomerization rather than static disorder. The difference Fourier map suggests a double-minimum potential for the proton tautomerism. Rapid tautomerization in [²H₈]toluene solution can be observed by ¹H NMR spectroscopy down to −90 °C, just above the melting point of the solvent.

To date crystal structures of dibenzo[b,i][1,4,8,11]tetraaza-[14]annulene or 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraaza-cyclotetradecine (taa) and its derivatives and their metal complexes have been investigated with considerable interest (Fig. 1).[1-8] All complexes of tetramethyltaa (tmtaa) and tmtaa free base have a remarkable saddle shape because of steric interactions between the methyl groups and the o-phenylene rings, as shown in Fig. 2, while the molecular structures of dimethyltaa (dmtaa) and dimethyldixylene (dmdxtaa)[2] are planar. Also the structure of taa prepared by vacuum sublimation at 250 °C is planar.[1] The radius of the central 'hole' formed by the four nitrogen atoms in tmtaa is 1.90 Å, whereas the average of those for dmtaa and dmdxtaa is 1.92 Å. There appears to be a correlation between the molecular planarity of the macrocycles and their hole sizes. Hoard has suggested that, if the radius of the central hole of the porphyrin is less than 1.96 Å, this macrocycle undergoes buckling to lead to S_4 form instead of a planar structure.[9] This was exemplified with [P(OH)₂(tpp)]-(OH)·2H₂O (H₂tpp = 5,10,15,20-tetraphenylphorphyrin) and [PCl₂(tpp)]Cl·CH₂Cl₂.[10,11] The macrocyclic hole size is crucial to the molecular structure and to the spectroscopic and thermodynamic properties of its metal complexes. Very interestingly, all molecules of taa and its derivatives reported so far show substantial alternation on the bond lengths in 1,3-propanediiminato linkages, which indicates incomplete π-conjugation within the linkages.

We have been interested in the correlation between spectroscopic properties and molecular structures of five-coordinated transition metal complexes.[12] During the course of these studies, single crystals of taa have been prepared of suitable quality for X-ray crystallography by recrystallization from xylene. This crystal has been proven to be a different crystal modification from that reported previously.

Honeybourne has shown the equivalency of the α,γ-carbon atoms in the propanediiminato linkage of the taa family by ¹H NMR experiments in solution, indicating the hydrogen bonding as N ··· H ··· N within the linkage due to the full π-conjug-

ation.[13] On the other hand, the solid state imine–enamine tautomerization of taa and its derivatives has been of considerable interest.[14,15] By means of ¹⁵N CPMAS–NMR Limbach et al.[15] have observed that the proton transfer in saddle-shaped tmtaa is much faster than that in coplanar dmtaa. Furthermore, the tautomeric states 3 and 4 in Fig. 1 were not significantly populated in dmtaa, while all four tautomers 1–4 were observed in tmtaa.

The crystals of dmtaa ($P2_1/n$, $R_w = 0.056$), dmdxtaa ($P2_1/n$, 0.087), tmtaa ($P\bar{1}$, 0.091) and taa ($P2_1/c$, 0.088) were reported to show substantial bond alternation in the respective propane-diiminato linkages (Fig. 3). The latter two crystals showed disordered amino-hydrogen positions but the former two did not. It was expected in the X-ray crystallographic study that the dynamic imine–enamine tautomerization would be observed as an apparent disorder of the hydrogen positions. The dynamic imine–enamine tautomerization reduces the degree of the bond alternation. The structural analysis of the present crystal modification of taa exhibits almost equal hydrogen distribution among the four nitrogen atoms and no bond alternation in the propanediiminato linkage at $R_w = 0.036$. This R_w may be close enough to the R factor to discuss the proton disorder in detail, whereas much larger than this are the R_w factors of the above-mentioned crystals which are all of the free bases of the taa family whose crystal structures have been reported. Here we describe additional support for the rapid imine–enamine tautomerization of taa obtained by ¹H NMR measurements for the [²H₈]toluene solution down to −90 °C (the melting point of the solvent is −95 °C).

Experimental

Materials and NMR Measurements.—Following the procedure of Hiller et al.,[16] taa was prepared and purified by recrystallization from N,N-dimethylformamide (DMF) as glittering red fine needles. These needles were further recrystallized as plates by slow evaporation of xylene solvent at ambient
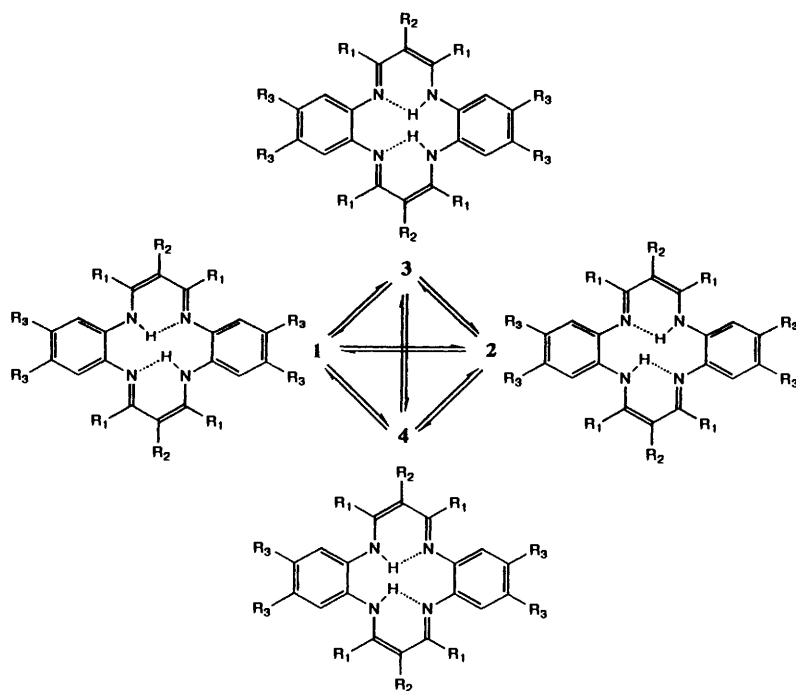
Fig. 1 Chemical structures and four possible tautomeric forms of dibenzo[b,i][1,4,8,11]tetraaza[14]annulenes. taa: $R_1 = R_2 = R_3 = H$; dmtaa: $R_1 = R_3 = H$, $R_2 = CH_3$; tmtaa: $R_1 = CH_3$, $R_2 = R_3 = H$; dmdxtaa: $R_1 = H$, $R_2 = R_3 = CH_3$.
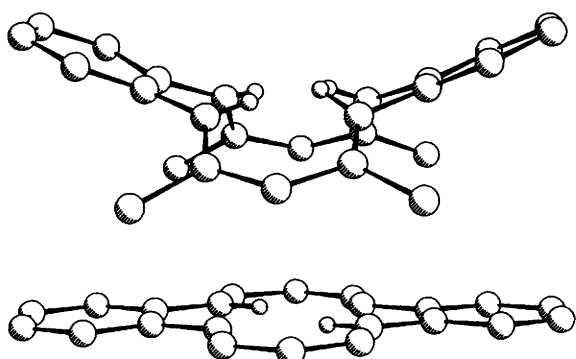

Fig. 2 Side view of the molecular structures of tmtaa[3] (top) and taa in the previously reported crystal modification (bottom).[1] Out of four disordered hydrogen positions of taa only two coordinates were communicated. All the peripheral and methyl hydrogen atoms are omitted.
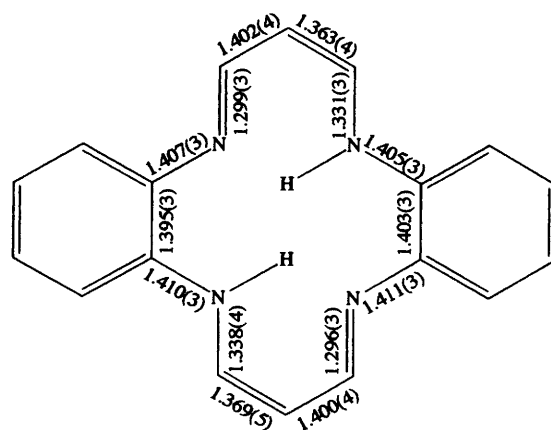

Fig. 3 Bond lengths of taa in the reported crystal modification.[1] Compare the bond alternation in the propanediiminato linkages of this molecule with those of the taa molecules in the present crystal modification shown in Fig. 6.

temperature, which were used for the X-ray diffraction and NMR measurements. [²H₆]Dimethyl sulfoxide ([²H₆]DMSO) and [²H₈]toluene were used as solvents for the NMR measurements at room and various temperatures, respectively. The ¹H NMR spectra were recorded on a JEOL JNM-EX400 (400 MHz) spectrometer and chemical shifts were reported in ppm from the internal signal due to protons in the solvent (taking δ = 2.100 for CH₃ in [²H₈]toluene).

Crystal Data.—C₁₈H₁₆N₄, M = 288.35, monoclinic, a = 14.926(2), b = 5.2342(8), c = 19.570(2) Å, β = 112.195(7)°, V = 1415.6(6) Å³, (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range 45.1 ≤ 2θ ≤ 54.7°, 298 K, Cu-Kα radiation, λ = 1.5418 Å), space group P2₁/a (no. 14), Z = 4, Dₑ = 1.353 g cm⁻³, F(000) = 608. Red plate crystals. Crystal dimensions 0.50 × 0.33 × 0.05 mm, μ(Cu-Kα) = 6.19 cm⁻¹.

Data Collection and Processing.—Rigaku AFC5R diffractometer, 298 K. Reflections with 4.7 ≤ 2θ ≤ 139.9° were measured with graphite monochromatized Cu-Kα radiation from a fine-focus anode of 12 kW-type rotating-anode generator. The ω–2θ scan mode with scan rate 16°/min (in ω) was applied for 2613 reflections (0 ≤ h ≤ 16, 0 ≤ k ≤ 5, − 21 ≤ l ≤ 20), 2364 unique (merging R = 0.013 after absorption correction), giving 1443 with I ≥ 3.00σ(I) which were labelled observed, and used in the structure refinement. Two rescans were applied for weak reflections. The scan width was Δω = (1.42 + 0.25tanθ)°. Corrections were made for Lorentz and polarization factors. Three standard reflections monitored at every 150 reflections showed only statistical changes in intensity (≤ 0.10% intensity loss). Semiempirical correction for the absorption was made based on azimuthal (ψ) scans for three selected reflections.[17] The transmission factors were 0.88–1.00.

Structural Analysis and Refinement.—The structure was solved by the direct method using SIR88 program.[18] The coordinates of all the atoms and the anisotropic and isotropic thermal parameters for the non-hydrogen and hydrogen atoms, respectively, were refined by full-matrix least-squares procedure based on F with weight $w = 1/\sigma^2(F_o)$. The secondary extinction coefficient (75.1×10^{-7}) and the anomalous dispersion were considered in the final stage of the refinement. At convergence, $R = 0.033$, $R_w = 0.036$, S (goodness-of-fit) = 1.61, reflection/parameter ratio = 5.31, max-shift/error ratio = 0.00, and residual electron densities = -0.13–0.11 e$^-$ Å^{-3}. All calculations were performed on a VAXstation 3200 computer with Rigaku/MSC TEXSAN software package[19] which used the atomic scattering factors (f, $\Delta f'$ and $\Delta f''$) taken from ref. 20. The relevant tables have been deposited at the Cambridge Crystallographic Data Centre (CCDC).†

Results and Discussion

Structure of Dibenzo[b,i][1,4,8,11]tetraaza[14]annulene.— The present crystal of taa is isostructural with those of Ni^{II} and Co^{II} complexes with deprotonated taa.[5] There are two independent molecules (**A** and **B**) in the unit cell. These molecules as well as dmtaa and dmdxtaa molecules are of central symmetry, while the previously reported crystal of taa does not show any molecular symmetry.[1] The molecular structure and numbering scheme are shown in Fig. 4. The molecules are remarkably coplanar, average atomic deviations from the molecular planes (defined by the non-hydrogen atoms) being 0.011 and 0.024 Å for **A** and **B**, respectively. The maximum atomic deviations from the molecular planes are 0.032(2) and 0.048(2) Å for N(1) and C(13), respectively. The average radius of the central hole 1.933 Å, which is obtained from the separations between the '*trans*' nitrogen atoms, is significantly larger than 1.902 Å in saddle-shaped tmtaa.

In the course of the refinement, positional disorder at the amino hydrogens was indicated for both **A** and **B**. At $R = 0.041$ ($R_w = 0.049$) for all the isotropically refined hydrogens other than the amino hydrogens, the difference Fourier maps on the planes defined by N(1/11), N(2/12) and C(9/19) were calculated, as shown in Fig. 5. Further refinement was carried out upon the fixed population of 1/2 for each disordered hydrogen. The resulting isotropic thermal parameters of the disordered hydrogens are 1.4(8)/5(1) and 1.2(4)/4(1) Å^2 for H(1N)/H(2N) and H(11N)/H(12N), respectively. Another refinement with a common fixed thermal parameter, $B_{iso} = 4.0$ Å^2 for all the disordered hydrogens, gave occupancy factors of 0.56/0.44 and 0.61/0.39 for the same hydrogen couples.

The quality of the reflection data necessary to the following arguments can be seen from the Fig. 5 where the profile and area of the positive-electron-density region in the central hole of **A** are respectively the same as those of **B**. The positive electron density due to the amino hydrogens does not point to the phenylenediamine but to the propanediiminato linkage. Besides, the positive electron densities at the disordered hydrogens are of similar value. The alternation of the bond lengths in the linkage group is not observed beyond the limit of $\Delta l < 3\sigma(l)$ (Fig. 6). According to the studies of Limbach *et al.*[14,15] both dmtaa and tmtaa molecules interconvert rapidly between the respective tautomers on the NMR time-scale in the crystals. Therefore, it is reasonably presumed that the present disorder does not arise from a mixture of static structures, where long- or short-range order of the respective two hydrogen orientations are present, but can be attributed to the proton tautomerism. The above
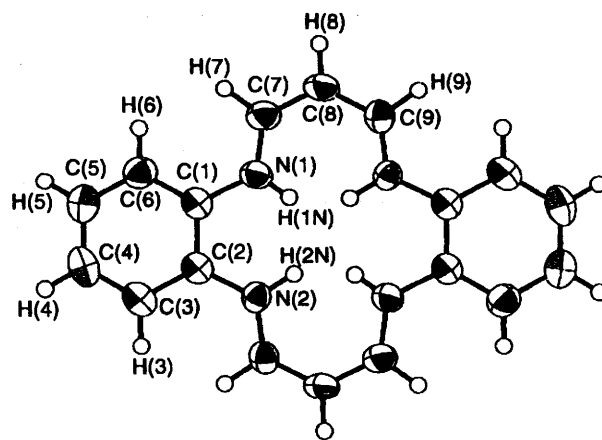
Fig. 4 Molecular structure of taa, together with atomic numbering scheme. Only the **A** molecule is shown since **B** has similar structure. The population of the hydrogens attached to the nitrogen atoms is referred to in the text. The atomic numbering for **B** is such that an X(10 + n) atom corresponds to an X(n) atom in **A**.

Fourier maps indicate the presence of two dominant interconverting tautomers 1 and 2 in Fig. 1, like dmtaa observed by ^{15}N CPMAS–NMR. The inequivalent occupancy factors for the amino hydrogens suggests an asymmetric double-minimum potential due to packing effects.

Selected bond distances and angles are shown in Fig. 6 and Table 1, respectively. All the bond distances are the same as those observed in the nickel(II) complex within the margin of error. However the bond distances in the propanediiminato linkages of the present taa are different from those in the reported taa where the bond alternation attributed to 1-amino-3-imino-1-propene structure has been observed. The average distance between the nitrogen atoms *trans* to each other in the nickel(II) complex is 3.740(4) Å, while that of taa is 3.867(6) Å. This elongation arises from the N–H···H–N nonbonding interaction (*vide infra*) and is responsible for the larger bond angles of N(1/11)–C(1/11)–C(2/12), C(1/11)–C(2/12)–N(2/12), C(1/11)–N(1/11)–C(7/17) and C(7/17)–C(8/18)–C(9/19) than those in the nickel(II) complex by 2–4°.

Remarkable bond alternation in the propanediiminato linkages has been observed for tmtaa and taa in the reported modification; the bond lengths in the N–C–C–C–N linkages of the former are: 1.317(2), 1.417(3), 1.377(3) and 1.343(3); 1.316(3), 1.411(3), 1.375(3) and 1.343(3) Å, respectively. The bond lengths of the macrocycles of the reported and present taa are shown in Figs. 3 and 6, respectively. The C–C bond lengths in the linkage of the present taa are the same as those in the phenylene group, and the C–N bond lengths in the same linkage are substantially shorter than those in the phenylenediamine group. The crystallographic evidence for the complete π-conjugation through the entire propanediiminato linkage of taa gives also support to the imine–enamine tautomerization.

A and **B** show less significant difference in the corresponding bond and torsion angles. The bond angles in the C–NH–CH= CH–CH=N–C moieties in both **A** and **B** range from 123.6(2) to 126.1(3)°, while those in tmtaa are 119.5(2) to 129.8(2)°. The average value of 129.5° for two C–NH–C bond angles in tmtaa is substantially larger than those in taa, which results from peripheral steric constraints. Nonbonding intramolecular H···H contacts between the respective methine protons and phenylene '*ortho*' protons range from 1.95 to 2.03 Å, while those at the periphery are of 2.25–2.39 Å. They may be distinguished by the NMR measurements at varying temperatures (*vide infra*).

The hydrogen bond distances for N(1/11)···H(2N/12N)

Table 1 Bond angles (°) for A and B molecules of dibenzo[b,i][1,4,8,11]tetraaza[14]annulene

A		B		tmtaa[a]
C(1)–N(1)–C(7)	123.9(2)	C(11)–N(11)–C(17)	124.5(2)	129.5(3)[b]
N(1)–C(7)–C(8)	123.9(3)	N(11)–C(17)–C(18)	124.1(2)	120.3(3)
C(7)–C(8)–C(9)	126.1(3)	C(17)–C(18)–C(19)	125.8(2)	127.3(3)
C(8)–C(9)–N(2')	124.4(2)	C(18)–C(19)–N(12')	124.5(2)	120.0(3)
C(9)–N(2')–C(2')	123.7(2)	C(19)–N(12')–C(12')	123.6(2)	125.4(3)[c]
N(1)–C(1)–C(2)	116.2(2)	N(11)–C(11)–C(12)	116.7(2)	117.4(3)
N(1)–C(1)–C(6)	124.0(2)	N(11)–C(11)–C(16)	123.7(2)	123.6(3)
N(2)–C(2)–C(1)	116.9(2)	N(12)–C(12)–C(11)	117.0(2)	117.6(3)
N(2)–C(2)–C(3)	124.6(2)	N(12)–C(12)–C(13)	124.7(2)	123.2(3)

[a] Average of the corresponding bond angles of tmtaa.[3] [b,c] These values are the averages of the C–NH–C (amine) and C–N=C (imine) bond angles, respectively.
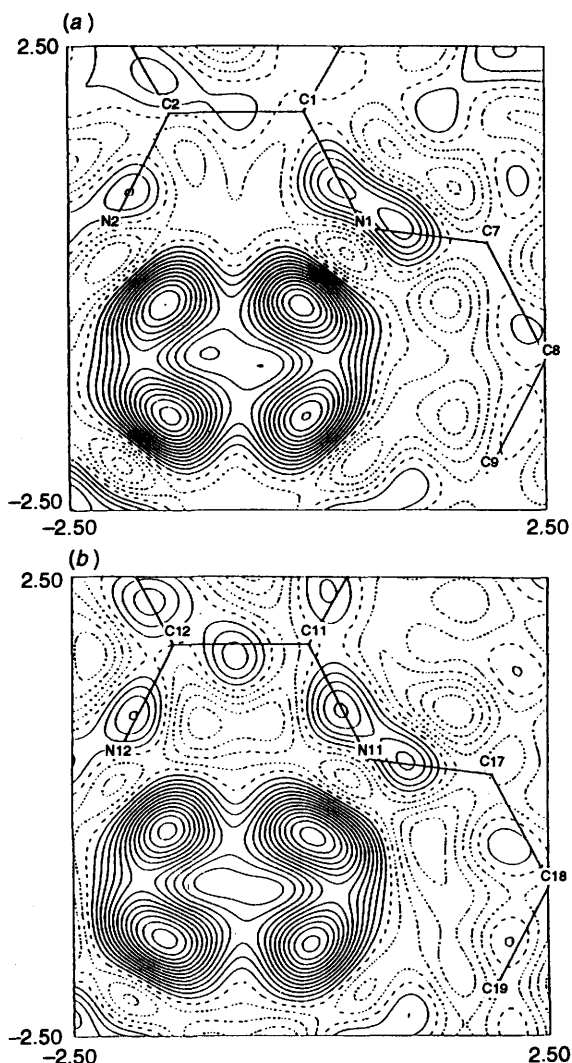

Fig. 5 Residual electron density maps on planes of 5 × 5 Å² area defined by the N(1/11), N(2/12) and C(9/19) atoms. All hydrogens other than amino hydrogens are included in the difference Fourier syntheses at $R = 0.041$ and $R_w = 0.049$. The contour interval is 0.02 e⁻ Å⁻³, and the solid and broken lines represent the positive and non-positive contours, respectively.
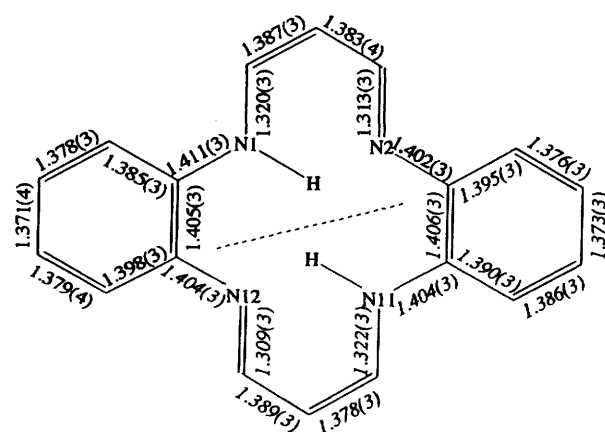

Fig. 6 Bond distances (Å) of taa. Those of A and B molecule are shown by roman and italic figures or by the figures in upper and lower part of the broken line, respectively.

and N(2/12)•••H(1N/11N), 2.08(5)–2.15(4) Å, are shorter than those across the phenylenediamine rings, 2.27(4)–2.32(5) Å. The latter distances seem to be shorter than those in tmtaa; 2.41(3) and 2.45(3) Å.[3] The relevant nonbonding H•••H contacts corresponding to 1 and 2 states are of 2.1 Å, while those to 3 and 4 are of 1.7 Å, which are smaller than the normal van der Waals contact of 2.0–2.4 Å.[21] Interestingly, the corre-

sponding values in tmtaa are longer than 1.7 Å, that is, 1.8 and 2.2 Å, which may allow the presence of tautomers 3 and 4. Moreover, the amino hydrogens of the coplanar taa family lie nearly in the N₄-plane (displacement of 0.04 Å), while those of non-planar one are directed out of the same plane (0.1 Å). Presumably the rate of the tautomerization is affected enormously by the nonbonding H•••H interaction due to this hydrogen displacement. It is therefore tempting to presume that the coplanar molecules exhibit a concerted double proton transfer but non-planar ones enable a nonconcerted double or single proton transfer.

N(2) and N(12) carry the hydrogens with larger isotropic thermal parameters $\{B[\text{H}(2\text{N})/\text{H}(12\text{N})] = 5/4 \text{ Å}^2\}$ than the others $\{B[\text{H}(1\text{N})/\text{H}(11\text{N})] = 1.8/1.2 \text{ Å}^2\}$. This may also suggest that the tautomers 1 and 2 are unequally populated, like dmtaa. The relevant asymmetric double-well potential should be attributed to the packing or solid state effects. However, any intermolecular contact cannot be clearly pointed out so as to correlate with this potential and with the (following) rhombic distortion of the central N₄-hole, where the 'trans' N(2/12)••• N(2'/12') contacts, 3.857/3.852 Å, are substantially shorter than the N(1/11)•••N(1'/11') ones, 3.872/3.885 Å, because no exceptional intermolecular contact is observed.

The space group of dmtaa and dmdxtaa with central symmetric molecular structure are $P2_1/n$ with $Z = 2$, and that of taa in the reported crystal modification is $P2_1/c$ with $Z = 4$. The molecular packing of these crystals can be typified in terms of the herringbone pattern which is often observed in crystals of macrocyclic complexes and free bases of this type of ligand. On the other hand, the present taa crystallizes into double herringbone pattern where one herringbone consists of A molecule with its centre of gravity on $z = 1/2$ and the other of B on $z = 0$, as shown in Fig. 7. The dihedral angle between the
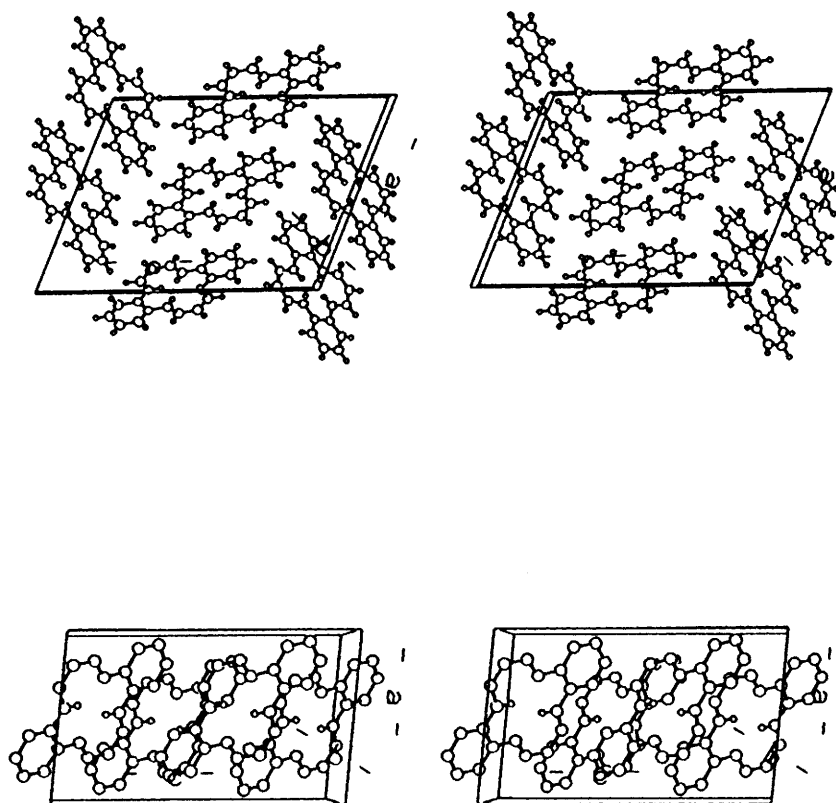
Fig. 7 Stereoviews along the respective *b* axes of the present (top) and reported (bottom) crystal modifications of taa.[1]

molecular planes of **A** and **B** is 52°, and those angles between neighbouring **A**'s and between **B**'s are 77 and 78°, respectively. In the reported taa crystal, the interplanar angle between the neighbouring molecules (related by the two-fold screw) is 88°. This larger interplanar angle may be one of the reasons why the calculated density of the reported crystal (1.333 g/cm³) is substantially smaller than that of the present crystal (1.353 g/cm³).

NMR of Dibenzo[b,i][1,4,8,11]*tetraaza*[14]*annulene.*—The ¹H NMR spectrum of taa observed at room temperature consists of three triplets (T_1, T_2 and T_3) and a pair of six-line structures. This paired structure can be attributed to the AA'XX' phenylene spin system, although the ideally resolved spectrum is of a pair of ten-line structures. The chemical shifts in the [²H₈]toluene solution are δ_A = 6.73 and δ_X = 6.65, which seem to be shifted upfield compared with ordinary aromatic protons. They are increased respectively to δ 7.25 and 6.91 in [²H₆]DMSO solution, which recalls the aromatic solvent induced shift.

T_1, T_2 and T_3 can be assigned to the –CH–N···H··· N–CH–, ···H···N–CH–CH–CH–N···H··· and N–CH– CH–CH–N protons, respectively.[13] The observed intensity ratio is $T_1:T_2:T_3$ = 1:2:1 and for all triplets J = 6 Hz in [²H₈]toluene and [²H₆]DMSO solution. Therefore, the rapid imine–enamine tautomerization can be deduced in solvents with very different physicochemical properties, such as proton affinity and dielectric constant.

A diamagnetic ring current is anticipated in a $(4n + 2)\pi$ system,[22] while a paramagnetic ring current can be expected for taa with a $4n\pi$ system.[23] [18]Annulene showed chemical shifts at 9.25 and −4.22 for the peripheral and inner protons, respectively, whereas for [16]annulene these are at δ 5.2 and 10.3.[24] The δ value of T_3 is 4.70 or 5.06 in the [²H₈]toluene or [²H₆]DMSO solution, respectively. Hence, the upfield shifts of the phenylene protons of taa can be rationalized. This reason

also explains the large downfield shift for the inner amino proton and the contribution of the deshielded proton structure in the tautomerization. Actually the chemical shift of the amino proton (δ = 13.96) is shifted much more downfield than that (δ = 9.27 in CDCl₃) of 7,8,15,16,17,18-hexahydrodibenzo-[b,j][1,4,8,11]tetraazacyclotetradecine where the macrocyclic π-conjugation cannot be expected, although similar tautomerization is present.[25]

The temperature-dependent (*T*-dependent) chemical shifts in the [²H₈]toluene solution are shown in Fig. 8. All the T_1, T_2, T_3 and AA'XX' constituent spectra observed at −90 °C have the same spectral patterns as those obtained at 20 °C, indicating rapid tautomerization even at low temperatures. The δ value for the methine protons adjacent to the respective nitrogen atoms shows upfield *T*-dependent shift, as the temperature is decreased. The *T*-dependent shift of the higher-field signal due to the phenylene protons exhibits an upfield shift to a similar extent as that of the above methine protons (0.0011 and 0.0015 ppm K⁻¹). This similarity may result from the same stem and this phenylene signal may be assigned to the *ortho* proton. Two protons in N–CH–CH–CH–N have the short H···H contacts to the respective *ortho* phenylene protons (*vide supra*), which gives rise to the deshielding of these protons. Deexcitation of some of the molecular vibration modes may reduce the deshielding; 290 K corresponds to 200 cm⁻¹. The δ values are consequently shifted upfield with decrease of temperature. The methine proton in N–CH–CH–CH–N does not show all dependent shift (δ = 4.70) and another signal due to the phenylene protons also exhibits little *T*-dependence. The atomic displacement of the amino hydrogens from the N_4-plane (*vide supra*) may be decreased with decreasing temperature. The downfield shift of these protons should increase with decrease in the atomic displacement,[23b,26] to which the *T*-dependence (−0.0031 ppm K⁻¹) of this chemical shift may be attributed. The δ value of the amino proton in [²H₆]DMSO is shifted upfield from that in [²H₈]toluene, while all the other
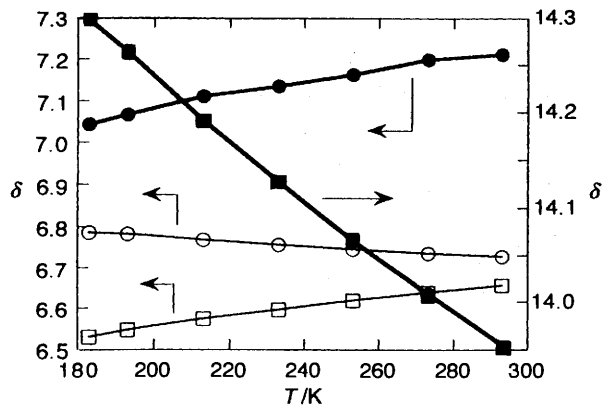
Fig. 8 Temperature dependence of the chemical shifts of taa observed in [$^2H_8$]toluene. Because the signal due to the N–CH–CH–CH–N proton does not show significant temperature-dependent shift (δ = 4.70), its temperature dependence curve is omitted from the graph. (●), N–CH–CH–CH–N; (○), Ar-H (m); (□), Ar-H (o); N–H (■).

signals are shifted downfield. This finding may support the above idea because this solvent has a proton-attractive nature.

Acknowledgements

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