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# Structure determination of *N*-phenylcarbazole from semi-empirical quantum chemical calculations. Extent of twisting between the carbazole and phenyl moieties

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**ABSTRACT** The geometrical structures of *N*-Phenylcarbazole (NPC) have been determined using various semi-empirical quantum chemical methods. Optimizations of these structures were carried out using MNDO, MINDO/3, AM1 and PM3 Hamiltonians. The geometry of the predicted structures is discussed in terms of the extent of twisting of the two aryl moieties and where possible, the calculated results are compared with data obtained from supersonic jet studies and crystal analysis of NPC.

**ABSTRAK** Struktur-struktur geometri untuk *N*-Phenylcarbazole (NPC) telah ditentukan dengan menggunakan beberapa teknik separa empirik kimia kuantum. Pengoptimuman struktur-struktur ini dijalankan dengan menggunakan Hamiltonian-Hamiltonian MNDO, MINDO/3, AM1 dan PM3. Struktur-struktur yang diperolehi dalam pengiraan-pengiraan ini dibincangkan dalam konteks kebolehan kedua-dua unit aril dalam NPC untuk berputar antara satu sama lain. Keputusan-keputusan yang diperolehi dari pengiraan-pengiraan ini juga dibandingkan dengan data-data eksperimental dari spektroskopi jet supersonik dan struktur-struktur kristal sinar-X NPC.

(semi-empirical, *N*-Phenylcarbazole, twist angle)

## INTRODUCTION

The spectroscopic properties of carbazole have been extensively studied for the past 25 years. The interest in carbazole (Fig. 1a) derives from the fact that carbazole plays an important role as a chromophore in polymeric systems such as poly(*N*-vinylcarbazole) (PVK). Carbazole has been studied in polymeric systems [1] as well as under isolated conditions in microcrystals, Shpolskii matrices [2,3] and supersonic jet expansion [4]. Detailed theoretical studies of carbazole have also been carried out to complement the experimental results [5-7]. Carbazole exhibits a relatively strong proton-donating behaviour which has been attributed to the depletion of electron density on the nitrogen(N9) atom

[7]. Other interesting properties have been observed when the hydrogen on this nitrogen is replaced by chromophoric groups, one of which is the "Twisted Intramolecular Charge Transfer" (TICT) state [8,9]. Generally, TICT states form when two moieties, a donor and an acceptor, that are separated by a  $\sigma$  bond undergo a charge transfer process coupled with a twisting. This coupling effect is partly determined by the initial twisting angle of the two moieties [14]. It is thus important to determine the initial geometry of the TICT forming species to understand better the TICT process. TICT state formation was first reported for dimethylaminobenzonitrile [10]. This phenomena is observed almost

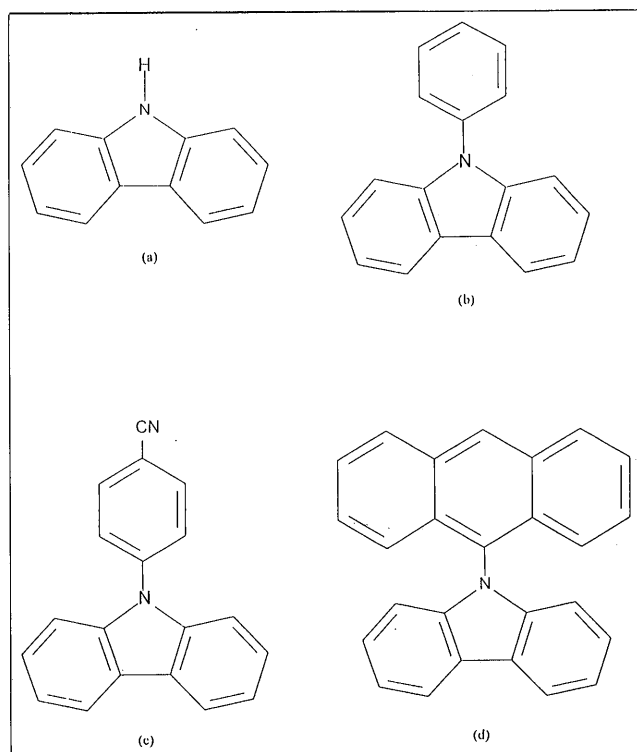


Figure 1. Structures of (a) carbazole, (b) *N*-phenylcarbazole, (c) cyanophenylcarbazole and (d) 9-anthrylcarbazole.

exclusively in polar solutions although there are a small number of compounds that have been reported to exhibit TICT fluorescence in non-polar solutions [11] and under isolated conditions [12]. Various substituted carbazoles such as cyanophenylcarbazole (CPC) (Fig. 1c) [13] and 9-anthrylcarbazole(9AC) (Fig. 1d) [14] exhibit TICT state formation in polar solutions.

Laser-induced fluorescence (LIF) studies carried out under isolated conditions have shown that the vibronic spectral features of carbazole, CPC and NPC (Fig. 1b) are very similar [15]. The electronic origins of CPC and NPC are observed to be red shifted with respect to the electronic origin of carbazole. TICT state formation, which is characterized by a broad red-shifted fluorescence, is not observed for CPC in supersonic jet expansion [16].

Interestingly, NPC does not form TICT state even in polar solution [13] although it exhibits spectral features similar to those of CPC in supersonic expansion. This anomalous behaviour prompted our preliminary study on the ground state structures of NPC by the use of semi-empirical quantum chemical tools. Our results are compared with reported experimental data.

## COMPUTATIONAL DETAILS

The geometry of NPC was optimized using the general purpose semi-empirical molecular orbital package, MOPAC6 [17]. The geometrical structure of NPC to be input into the MOPAC6 program was built employing

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AM1 PRECISE GEO-OK HESS=1 RECALC=3 EF
npcfor.dat
npcfor.dat

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| i | a         | f | b          | f | c          | f | j  | k  | l  |       |
|---|-----------|---|------------|---|------------|---|----|----|----|-------|
| C | 0.0000000 | 0 | 0.0000000  | 0 | 0.0000000  | 0 | 0  | 0  | 0  | 0.000 |
| C | 1.3900127 | 1 | 0.0000000  | 0 | 0.0000000  | 0 | 1  | 0  | 0  | 0.000 |
| C | 1.3915090 | 1 | 118.770825 | 1 | 0.0000000  | 0 | 2  | 1  | 0  | 0.000 |
| C | 1.3990696 | 1 | 120.838456 | 1 | 0.0000000  | 1 | 3  | 2  | 1  | 0.000 |
| C | 1.4077358 | 1 | 121.364962 | 1 | 0.0000000  | 1 | 4  | 3  | 2  | 0.000 |
| C | 1.3785406 | 1 | 115.691976 | 1 | 0.0000000  | 1 | 5  | 4  | 3  | 0.000 |
| C | 1.3974757 | 1 | 108.304145 | 1 | 180.000000 | 1 | 6  | 5  | 4  | 0.000 |
| C | 1.3786888 | 1 | 108.462245 | 1 | 0.0000000  | 1 | 7  | 6  | 5  | 0.000 |
| N | 1.3997320 | 1 | 136.715765 | 1 | 180.000000 | 1 | 5  | 4  | 3  | 0.000 |
| C | 1.3929776 | 1 | 127.399879 | 1 | 180.000000 | 1 | 7  | 6  | 5  | 0.000 |
| C | 1.3899633 | 1 | 119.099753 | 1 | 180.000000 | 1 | 10 | 7  | 6  | 0.000 |
| C | 1.3912433 | 1 | 118.772102 | 1 | 0.0000000  | 1 | 11 | 10 | 7  | 0.000 |
| C | 1.3987941 | 1 | 120.784042 | 1 | 0.0000000  | 1 | 12 | 11 | 10 | 0.000 |
| C | 1.4400866 | 1 | 125.913345 | 1 | 0.0000000  | 1 | 9  | 5  | 4  | 0.000 |
| C | 1.4121349 | 1 | 123.282703 | 1 | 180.000000 | 1 | 14 | 9  | 5  | 0.000 |
| C | 1.3959807 | 1 | 123.666711 | 1 | 180.000000 | 1 | 15 | 14 | 9  | 0.000 |
| C | 1.3863101 | 1 | 120.472191 | 1 | 0.0000000  | 1 | 16 | 15 | 14 | 0.000 |
| C | 1.3863149 | 1 | 118.278845 | 1 | 0.0000000  | 1 | 17 | 16 | 15 | 0.000 |
| C | 1.3959834 | 1 | 120.471841 | 1 | 0.0000000  | 1 | 18 | 17 | 16 | 0.000 |
| H | 1.0870402 | 1 | 122.018872 | 1 | 0.0000000  | 1 | 15 | 14 | 9  | 0.000 |
| H | 1.1035632 | 1 | 119.936737 | 1 | 180.000000 | 1 | 16 | 15 | 14 | 0.000 |
| H | 1.1027006 | 1 | 120.859873 | 1 | 180.000000 | 1 | 17 | 16 | 15 | 0.000 |
| H | 1.1035605 | 1 | 119.590525 | 1 | 180.000000 | 1 | 18 | 17 | 16 | 0.000 |
| H | 1.0870451 | 1 | 114.317404 | 1 | 180.000000 | 1 | 19 | 18 | 17 | 0.000 |
| H | 1.1010676 | 1 | 119.883920 | 1 | 180.000000 | 1 | 1  | 2  | 3  | 0.000 |
| H | 1.1028688 | 1 | 120.617203 | 1 | 180.000000 | 1 | 2  | 1  | 3  | 0.000 |
| H | 1.1036229 | 1 | 119.426878 | 1 | 180.000000 | 1 | 3  | 2  | 1  | 0.000 |
| H | 1.0924182 | 1 | 114.739771 | 1 | 180.000000 | 1 | 4  | 3  | 2  | 0.000 |
| H | 1.1011100 | 1 | 121.083941 | 1 | 0.0000000  | 1 | 10 | 7  | 6  | 0.000 |
| H | 1.1028742 | 1 | 120.617625 | 1 | 180.000000 | 1 | 11 | 10 | 7  | 0.000 |
| H | 1.1036135 | 1 | 119.453814 | 1 | 180.000000 | 1 | 12 | 11 | 10 | 0.000 |
| H | 1.0924013 | 1 | 114.735977 | 1 | 180.000000 | 1 | 13 | 12 | 11 | 0.000 |

Figure 2. MOPAC input file in internal coordinates of NPC.

Table 1. Selected dihedral angles of NPC for AM1, PM3, MINDO/3 and MNDO. Values obtained from X-ray experiments are also included.

| Dihedral angles(°)             | AM1    | PM3    | MINDO/3 | MNDO  | X-Ray                                 |
|--------------------------------|--------|--------|---------|-------|---------------------------------------|
| C15-C14-N9-C5<br>(twist angle) | 135.13 | 160.46 | 90.00   | 89.99 | 78.4 <sup>a</sup> , 54.8 <sup>b</sup> |
| C14-N9-C5-C4                   | 1.17   | 16.84  | 0.00    | 0.01  | -                                     |

a. Structure (a) from ref. [ 27].

b. Structure (b) from ref. [ 27].

the InsightII [18] builder module and was partially minimized using the CVFF force field method [18]. The NPC structure was then represented as internal coordinates (MOPAC6 *Z-matrix*) for input into the MOPAC6 program. A typical input file for geometry optimization jobs is depicted in figure 2. It contains, besides a description of the molecular geometry in MOPAC6 internal coordinate, a set of keywords to specify the required calculations and the output format. The first keyword used in the input file specifies the Hamiltonian to be used in the calculation. In this case, the AM1[19] Hamiltonian is to be used in the run. PRECISE specifies that the default criteria for terminating all optimizations is to be increased by a factor of 100. MOPAC6 run will normally stop when the distance between any two atoms in the structure are within 0.8 Angstroms. The GEO-OK keyword overrides this. The EF keyword will prompt MOPAC6 to employ the eigenvector following routine in the optimization. Optimizations can be made to run faster by specifying the HESS=1 keyword. This will result in the calculation of the Hessian matrix before a particular geometry is optimized. RECALC=3 is used in conjunction with HESS=1 so that a new Hessian is calculated every 3 steps of the EF optimization.

The rest of the input file describes the molecular geometry of NPC in terms of internal coordinates. Note that all the indices in the fifth row of figure 2 are not included in the actual input *Z-matrix*. They are there to ease the understanding of the *Z-matrix*. The molecular geometry of NPC is defined in terms of the bond lengths (column a) between two atoms, bond angles (column b) between three atoms and dihedral angles (column c) defined by four atoms. Indices *i*, *j*, *k* and *l* are used to signify atoms under consideration in the *Z-matrix*. The bond length is defined between an atom *i* with an already defined atom *j*. The bond angle between atoms is defined between atom *i*, atom *j* and an already defined

atom *k*. Finally, the dihedral angle is defined between atoms *i*, *j*, *k* and an already defined atom *l*. The index *f* is a flag associated with each geometrical parameter of NPC. Bond lengths, bond angles and dihedral angles in NPC each have a flag *f* to the right of their columns. If the flag is set to 1, it signifies that the associated parameter is to be optimized. If set to 0, this parameter is to be constrained in the molecular optimization. In this paper, full geometrical optimizations were also carried out using MINDO/3[20], MNDO[21] and PM3[22] Hamiltonians. Visualisation of resulting structures was carried out using the InsightII Viewer module. Plotting of these geometrical structures were made with the PLUTON [28] program.

All MOPAC6 calculations were carried out either on a Silicon Graphics Iris Indigo workstation running IRIX 5.3 operating system or on the CRAY EL running Unicos operating system situated at the Faculty of Computer Science, UTM. All visualisation work were carried out on the Silicon Graphics Indigo.

## RESULTS AND DISCUSSION

As had been mentioned earlier, an important structural feature in understanding the spectroscopic behaviour of NPC in relation to the TICT state formation is the extent of twisting of the two ring moieties. NPC is a biaryl compound where both the phenyl and carbazole moieties are relatively free to rotate around the  $\sigma$  axis. This relative freedom is reflected in the different structures of the optimized NPC geometries predicted by the Hamiltonians employed in the calculation. Table 1 shows the selected parameters of optimized geometries for all four Hamiltonians. Numbering scheme of NPC molecule is shown in Fig. 3. The structures calculated by MINDO/3, MNDO, AM1 and PM3 are depicted in Figs. 4 to 7 respectively.

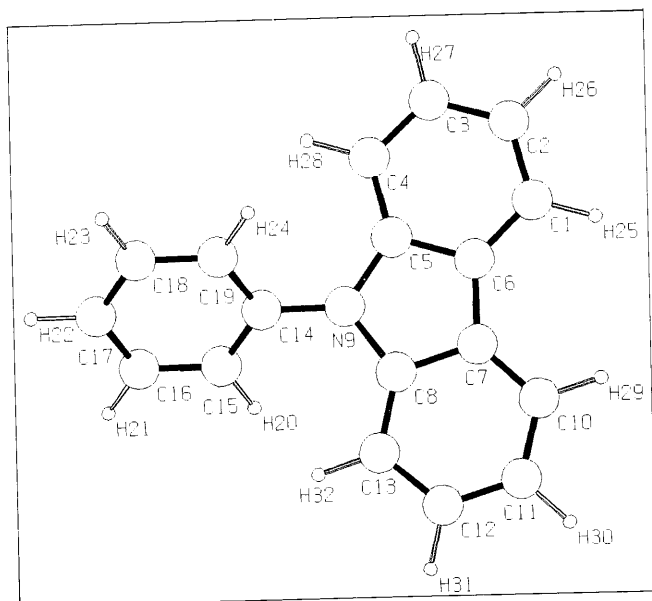


Figure 3. Numbering scheme of the atoms in NPC.

All the predicted structures give non-planar conformation for the NPC molecule. This is quite understandable considering the fact that a co-planar conformation between the two rings will result in an increase in steric hindrance caused by periplanar repulsions between the ortho-hydrogens on the phenyl ring and the nearest hydrogens on the carbazole moiety. However, it is observed that although from chemical intuition we would expect a perpendicular or near perpendicular geometry to be the most preferred structure, AM1 and PM3 Hamiltonians predict only partially rotated structures as the most stable ones. On the contrary, MINDO/3 and MNDO do predict perpendicular structures.

The structures of NPC ground state predicted by AM1 and PM3 Hamiltonians give  $C_1$  symmetry conformations. For AM1 and PM3, the C15-C14-N9-C5 dihedral angles representing the twist angles between the carbazole and phenyl planes are  $44.9^\circ$  and  $19.5^\circ$  respectively. Although PM3 seemed to suggest a stable structure at near-planar conformation, the in plane C14-N9-C5-C4 dihedral angle for PM3 is observed to be about  $17^\circ$ . For AM1, this dihedral angle is about  $1.2^\circ$ . The  $\sigma$  bond between the phenyl and the carbazole moiety is somewhat bent relative to the carbazole plane giving indication that there is a slight extent of nitrogen pyramidalization. Structures of carbazole calculated using PM3 and AM1 [23] also give bent N-H bonds whereas ab initio calculations [26] suggested a co-planar N-H bond. This discrepancy is a result of a known

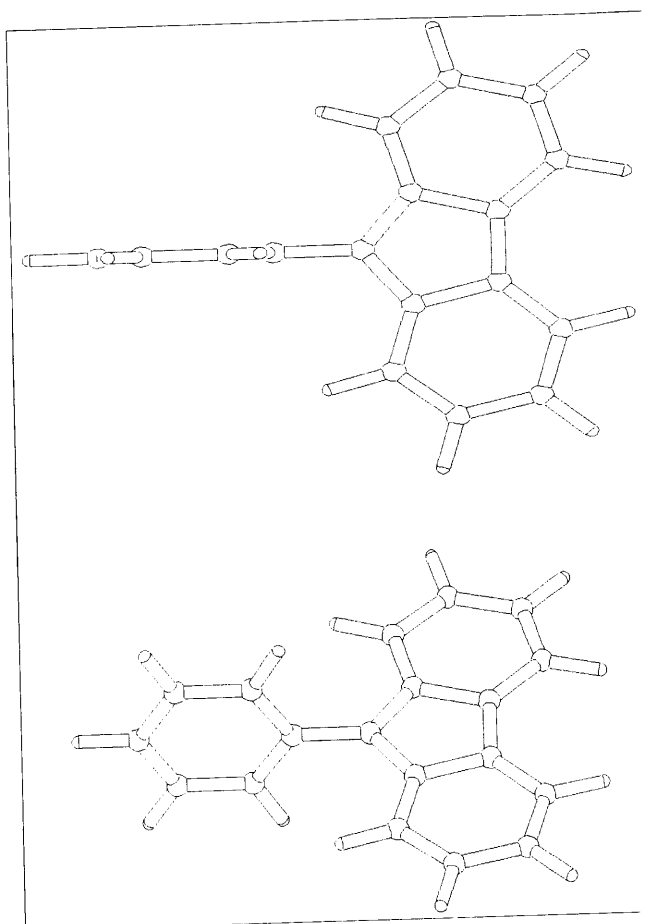


Figure 4. NPC structure predicted by MINDO/3 Hamiltonian.

error in PM3 [28] and is also observed to a smaller extent in the AM1 structure. This pyramidalization seems to play a part in determining the extent in which the two moieties are able to twist to get to the most stable configuration. With bent N9-C5 bonds, structures calculated using PM3 and AM1 Hamiltonians are able to reduce steric hindrance owing to periplanar repulsions of hydrogen and reach minimum energy configuration with only a moderate twisting of the two chromophoric moieties.

From Table 1, it can be seen that both MINDO/3 and MNDO Hamiltonians predict perpendicular structures. The C15-C14-N9-C5 twist angle of MINDO/3 and MNDO structures are both  $90.0^\circ$ . It is also observed that there is practically no bending of the C14-N9 bond relative to the carbazole moiety in both MINDO/3 and MNDO structures, indicating a lack of pyramidalization. This lack of pyramidalization can be attributed to the delocalization of electrons over the carbazole ring structure which involves the lone pair

electron on the N9 heteroatom and is consistent with the calculated depletion of electron density on N9 [7]. As a result, N9 is unable to retain  $sp_3$  hybridization and loses its pyramidal conformation. The predicted perpendicular structures of MINDO/3 and MNDO are consistent with the results obtained from supersonic jet studies of NPC [24]. Supersonic jet spectroscopy allows one to study a molecule in isolation from the various intermolecular forces. It is observed that the vibronic features of carbazole and NPC under isolated conditions are very similar. An insight that can be taken from this similarity is that the carbazole moiety in NPC is only minimally perturbed by the phenyl ring, thus inferring a non-planar structure. A non-planar structure allows very little conjugation between the carbazole and the phenyl rings, thus retaining an 'almost carbazolic'

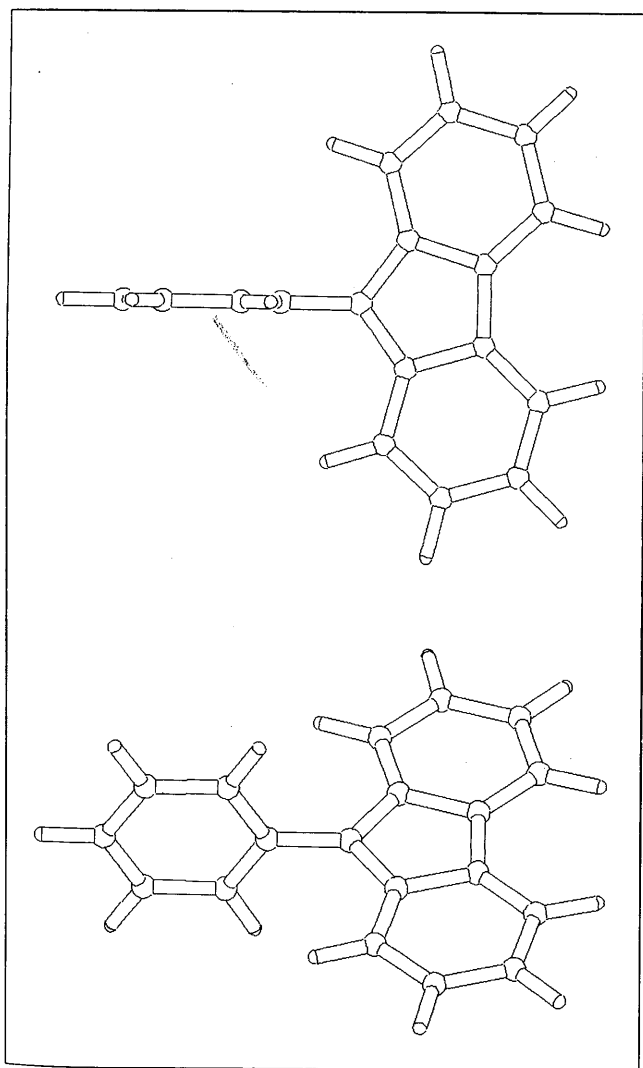


Figure 5. NPC structure predicted by MNDO Hamiltonian.

behaviour in the NPC electronic excitation. From symmetry considerations, non-planar  $C_1$  structures as predicted by AM1 and PM3 Hamiltonians will allow almost all vibronic transitions in the singlet ground state to the first singlet excited state electronic transition ( $S_0 \rightarrow S_1$ ) manifold and they would be expected to give fairly complex spectral structures. This was not observed in the vibronic spectrum of isolated NPC [24]. On the other hand, NPC with a perpendicular  $C_{2v}$  symmetry conformation will allow only certain vibrational modes to occur within the electronic transition manifold. This is consistent with the observed spectrum of isolated NPC [24]. Similar spectroscopic results were obtained for CPC [25] where its spectral features are somewhat similar to NPC and carbazole. It is thus expected that CPC will have a fairly similar perpendicular structure, at least in isolated conditions. It can be argued that under these conditions, CPC and NPC have perpendicular structures but the twisting and charge transfer processes that occur upon excitation for both molecules cannot be stabilized owing to lack of polar environment. For CPC, 'back charge transfer' could occur, lowering the high polarization needed for TICT formation. For NPC, high charge polarization between the carbazole and the phe-

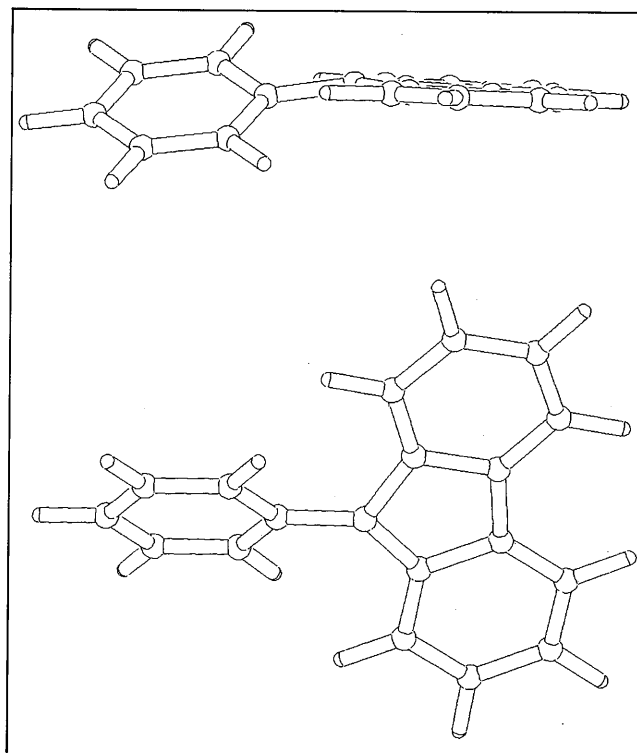


Figure 6. NPC structure predicted by PM3 Hamiltonian.

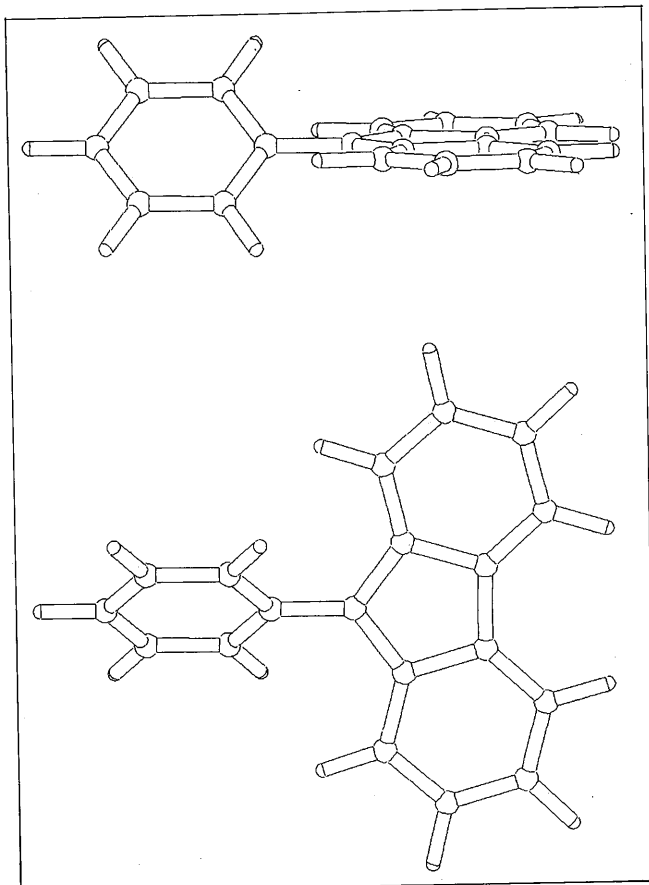


Figure 7. NPC structure predicted by AM1 Hamiltonian.

nyl moiety necessary for the formation of TICT state cannot be reached in the first place.

From the predictions concerning the extent of twisting of the two chromophoric moieties, MNDO and MINDO/3 have demonstrated results which are consistent with experimental data of isolated NPC. Pyramidalization is not observed in the structures and this is consistent with the calculated geometry of carbazole [26]. The PM3 structure is seen to be erroneous due to this pyramidalization. The AM1 structure also exhibits a slight pyramidalization where the C14-N9-C5-C4 dihedral angle is about  $1.2^\circ$ . Notwithstanding this, the structure predicted by AM1 Hamiltonian, with regard to the twisting of the two moieties, agrees quite well with the X-ray structure of NPC [27]. In the crystalline state, NPC exists as two independent conformers in an asymmetric unit where these structures have least-squares C15-C14-N9-C5 dihedral angles (twisting angles) of  $78.4^\circ$  (a) and  $54.8^\circ$  (b) [27]. With appropriate scaling of the dihedral angle values, the AM1 structure seem to conform to the (b) structure while the perpen-

dicular structures predicted by MNDO and MINDO/3 can be said to conform to the (a) structure. Both have discrepancies of about  $11^\circ$  and  $10^\circ$  and this can be attributed to the fact that in crystal structures, molecules are subjected to various intermolecular forces in complying to certain packing requirements, creating appropriate crystal conformations of minimum energy which may be different from conformations of isolated molecules.

## CONCLUSIONS

The ability of the two chromophoric moieties in NPC to twist around the C14-N9 bond gave rise to non-planar structures predicted by all the Hamiltonians employed in this calculation. PM3 predicted the smallest C15-C14-N9-C5 dihedral angle with a rather extensive pyramidalization centred on the N9 heteroatom. This pyramidalization is known not to occur in carbazole due to the extensive delocalization of electrons which involves the lone pair on the N9 heteroatom. The same is thought to have occurred in NPC. However, ignoring the slight pyramidalization of the AM1 structure, it seems to conform to the (b) molecule in the crystal unit of NPC. MNDO and MINDO/3 Hamiltonians predicted perpendicular structures which agrees quite well with spectroscopic results. It is also observed that these perpendicular structures conform to the (a) molecule in the NPC crystal unit.

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