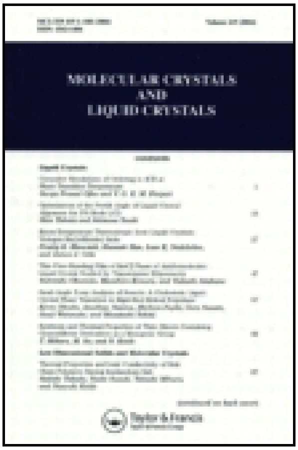

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Intermolecular Energy Calculations on Benzylideneaniline, Salicylideneaniline, MMBA and MMSA

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Intermolecular Energy Calculations on Benzylideneaniline, Salicylideneaniline, MMBA and MMSA

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Intermolecular energy minimizations have been performed on pairs of molecules of benzylideneaniline, salicylideneaniline, MMBA and MMSA to calculate the intermolecular interaction energies as well as the intermolecular orientation in these compounds.

Benzylideneaniline and salicylideneaniline can adopt a number of different orientations, which are close to energy. MMBA and MMSA have two orientations, close in energy, which are especially favoured. One is a "head-to-head" ordering and the other a "head-to-tail."

Keywords: energy minimisation, benzylideneaniline, salicylideneaniline

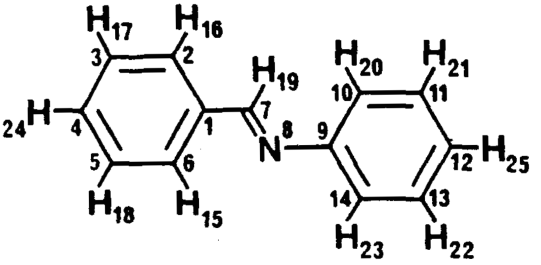
INTRODUCTION

Liquid crystals, incorporating schiff base units, have recently attracted much attention. Benzylideneaniline (BA), salicylideneaniline (SA), p-methoxy-benzylidene-N-(p-methylaniline) (MMBA) and p-methoxy-salicylidene-N-(p-methyl-aniline) (MMSA) represent model compounds of some of these liquid crystals, such as HOBACPC[1] and the MORA-series.[2]

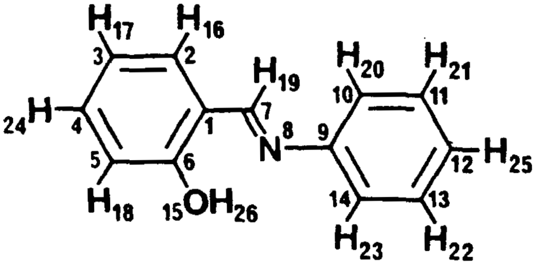
Knowledge of the ordering of the molecules and the interactions between them is important when trying to explain the behaviour of liquid crystals.

BA,[3-5] and to some extent, MMBA[6] have both been investigated from an experimental as well as a theoretical point of view. X-ray structure determinations have been performed on BA[7] and SA.[8]

In order to shed some light on the question of intermolecular ordering and interactions in liquid crystals, some minimizations have been carried out on pairs of BA, SA, MMBA and MMSA.



BA



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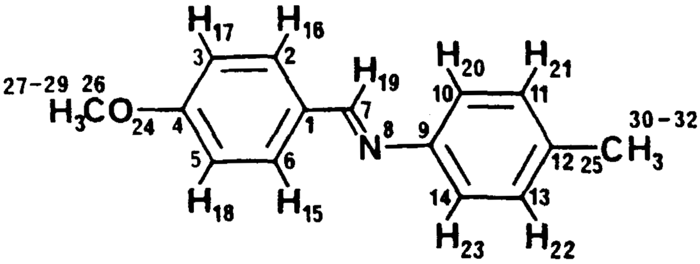
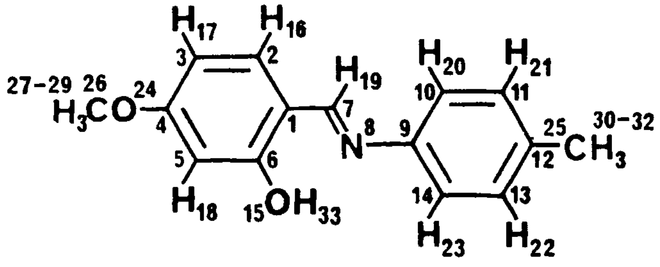


MMBA



MMSA

METHOD OF CALCULATION

The input structure (BA, SA, MMBA, MMSA) for the interaction calculations were completely optimized geometries obtained from AM1 calculations (Tables I–IV).

TABLE I

Geometry of BA (Ref. 14)

Atom *i*	Bond length (*i*-*j*)	Bond angle (*i*-*j*-*k*)	Dihedral angle (*i*-*j*-*k*-*l*)	*j*	*k*	*l*
1						
2	1.403			1		
3	1.392	120.28		2	1	
4	1.395	120.07	0.05	3	2	1
5	1.393	119.89	−0.02	4	3	2
6	1.400	119.40	−0.03	1	2	3
7	1.469	118.15	−179.88	1	2	3
8	1.291	123.06	−174.31	7	1	2
9	1.412	121.14	−179.19	8	7	1
10	1.412	123.22	35.32	9	8	7
11	1.391	120.50	176.71	10	9	8
12	1.393	120.41	0.28	11	10	9
13	1.394	119.66	−0.27	12	11	10
14	1.413	118.16	−147.99	9	8	7
15	1.101	120.24	179.96	6	1	2
16	1.100	119.93	180.05	2	1	6
17	1.099	119.90	180.05	3	2	1
18	1.100	119.98	179.99	5	4	3
19	1.115	113.54	5.16	7	1	2
20	1.100	120.16	−2.17	10	9	8
21	1.100	119.63	−179.63	11	10	9
22	1.100	119.85	−179.90	13	12	11
23	1.101	120.00	2.87	14	9	8
24	1.099	119.98	179.97	4	3	2
25	1.099	120.17	179.87	12	11	10

Bond lengths in Å and angles in degrees.

TABLE II

Geometry of SA (Ref. 14)

Atom i	Bond length (i-j)	Bond angle (i-j-k)	Dihedral angle (i-j-k-l)	j	k	l
1						
2	1.409			1		
3	1.385	121.35		2	1	
4	1.400	119.90	−0.00	3	2	1
5	1.383	120.26	−0.05	4	3	2
6	1.408	118.19	0.08	1	2	3
7	1.464	116.67	180.03	1	2	3
8	1.292	123.85	−177.50	7	1	2
9	1.410	121.71	−179.25	8	7	1
10	1.412	123.26	34.56	9	8	7
11	1.391	120.45	176.95	10	9	8
12	1.393	120.45	0.32	11	10	9
13	1.394	119.64	−0.36	12	11	10
14	1.413	118.10	−148.48	9	8	7
15	1.366	125.69	180.00	6	1	2
16	1.101	119.09	−179.87	2	1	6
17	1.099	120.19	180.02	3	2	1
18	1.099	121.48	180.02	5	4	3
19	1.115	113.32	1.95	7	1	2
20	1.100	120.20	−1.94	10	9	8
21	1.100	119.61	−179.68	11	10	9
22	1.100	119.85	−179.85	13	12	11
23	1.101	120.07	2.70	14	9	8
24	1.100	119.81	180.00	4	3	2
25	1.099	120.18	179.84	12	11	10
26	0.971	110.08	−0.38	15	6	1

Bond lengths in Å and angles in degrees.

A method similar to that of Caillet and Claverie,[9] was used for evaluating the intermolecular interaction energies.

The total interaction energy (E_{TOT}) is the sum of contributions of potential energies (E_P) and electrostatic energies (E_{EL}):

$$E_{TOT} = E_P + E_{EL} \tag{1}$$

The electrostatic energies (E_{EL}) were calculated from equation 2:

$$E_{EL} = \frac{C * \sum_{IJ} Q_I Q_J}{R_{IJ}} \tag{2}$$

where Q_I and Q_J are the atomic charges on atoms i and j, respectively, R_{IJ} is the interatomic distance and C is a conversion factor. The

TABLE III

Geometry of MMBA (Ref. 15)

Atom i	Bond length $(i\text{-}j)$	Bond angle $(i\text{-}j\text{-}k)$	Dihedral angle $(i\text{-}j\text{-}k\text{-}l)$	j	k	l
1						
2	1.405			1		
3	1.386	120.75		2	1	
4	1.409	119.24	0.02	3	2	1
5	1.399	120.60	0.00	4	3	2
6	1.399	119.36	0.00	1	2	3
7	1.467	118.19	−179.90	1	2	3
8	1.292	123.10	−175.34	7	1	2
9	1.411	121.16	−179.07	8	7	1
10	1.412	123.46	34.35	9	8	7
11	1.389	120.56	176.76	10	9	8
12	1.399	120.86	0.33	11	10	9
13	1.398	118.87	−0.36	12	11	10
14	1.412	118.16	−148.94	9	8	7
15	1.102	120.18	180.00	6	1	2
16	1.101	119.88	180.05	2	1	6
17	1.098	121.31	180.02	3	2	1
18	1.098	121.04	180.01	5	4	3
19	1.115	113.53	4.09	7	1	2
20	1.100	120.15	−2.15	10	9	8
21	1.100	119.66	−179.65	11	10	9
22	1.100	119.70	−179.86	13	12	11
23	1.101	119.94	2.82	14	9	8
24	1.379	114.78	180.00	4	3	2
25	1.480	120.09	179.80	12	11	10
26	1.423	116.25	179.92	24	4	3
27	1.119	103.39	−179.88	26	24	4
28	1.117	110.65	−61.34	26	24	4
29	1.117	110.66	61.58	26	24	4
30	1.117	111.37	180.04	25	12	11
31	1.118	110.26	−59.60	25	12	11
32	1.118	110.26	59.71	25	12	11

Bond lengths in Å and angles in degrees.

charges were calculated using both the CNDO/2 method[10] (BA, SA, MMBA and MMSA), the AM1 method[11] (BA) and *ab initio* methods (Gaussian 80, STO-3G)[12] (BA) on the geometries described earlier (see Tables I–IV for geometries and Table V for charges).

The potential energies were calculated using equation 3:

$$E_P = \sum_{IJ} \left(\frac{-A}{R_{IJ}^6} + BE^{(-CR_{IJ})} \right) \tag{3}$$

where A, B and C are atomic parameters and RIJ the interatomic distances.

TABLE IV

Geometry of MMSA (Ref. 15)

Atom *i*	Bond length (*i*-*j*)	Bond angle (*i*-*j*-*k*)	Dihedral angle (*i*-*j*-*k*-*l*)	*j*	*k*	*l*
1						
2	1.410			1		
3	1.380	121.94		2	1	
4	1.413	118.98	−0.03	3	2	1
5	1.391	120.93	−0.00	4	3	2
6	1.409	118.14	−0.08	1	2	3
7	1.462	116.75	180.05	1	2	3
8	1.292	123.88	−178.03	7	1	2
9	1.409	121.70	−179.17	8	7	1
10	1.412	123.38	34.05	9	8	7
11	1.389	120.59	176.88	10	9	8
12	1.399	120.82	0.29	11	10	9
13	1.398	118.87	−0.31	12	11	10
14	1.413	118.22	−149.08	9	8	7
15	1.365	125.50	179.94	6	1	2
16	1.102	118.96	−179.89	2	1	6
17	1.098	121.63	179.99	3	2	1
18	1.098	122.39	180.01	5	4	3
19	1.115	113.35	1.54	7	1	2
20	1.100	120.17	−2.07	10	9	8
21	1.100	119.66	−179.67	11	10	9
22	1.100	119.69	−179.91	13	12	11
23	1.101	120.05	2.80	14	9	8
24	1.376	114.76	179.99	4	3	2
25	1.480	120.09	179.89	12	11	10
26	1.424	116.38	179.96	24	4	3
27	1.119	103.32	179.98	26	24	4
28	1.116	110.59	−61.45	26	24	4
29	1.116	110.60	61.42	26	24	4
30	1.117	111.35	−179.70	25	12	11
31	1.118	110.32	−59.36	25	12	11
32	1.119	110.22	59.98	25	12	11
33	0.972	110.02	0.08	15	6	1

Bond lengths in Å and angles in degrees.

The energy minimization process was carried out using Chem-X.[13] Each molecule was assumed to be a rigid body. Both molecules were then rotated and translated with respect to a fixed coordinate system. Analytically calculated gradients were utilized. Several relative orientations were chosen as starting points for the minimization process.

The computations were carried out on either a VAX 11/785 or on a VAX 8600.

TABLE V

Charges in BA, SA, MMBA and MMSA

		BA		SA	MMBA	MMSA
Atom	AM1	CNDO/2	STO-3G	CNDO/2	CNDO/2	CNDO/2
1	−0.07	0.01	−0.01	−0.06	−0.01	−0.08
2	−0.10	0.01	−0.05	0.03	0.03	0.05
3	−0.13	0.01	−0.06	−0.02	−0.05	−0.08
4	−0.11	0.01	−0.05	0.04	0.19	0.21
5	−0.14	0.01	−0.06	−0.05	−0.06	−0.12
6	−0.08	0.01	−0.04	0.19	0.03	0.21
7	−0.01	0.11	0.06	0.13	0.12	0.13
8	−0.15	−0.16	−0.25	−0.18	−0.16	−0.19
9	−0.01	0.11	0.08	0.11	0.10	0.11
10	−0.15	−0.03	−0.06	−0.03	−0.03	−0.03
11	−0.12	0.02	−0.05	0.02	0.00	0.00
12	−0.13	−0.01	−0.06	−0.01	0.03	0.03
13	−0.12	0.02	−0.05	0.02	0.00	0.00
14	−0.10	−0.03	−0.05	−0.03	−0.03	−0.03
15	0.15	0.00	0.07	−0.25	0.00	−0.25
16	0.13	−0.01	0.05	−0.01	−0.01	−0.01
17	0.13	−0.01	0.06	−0.01	0.01	0.01
18	0.13	−0.01	0.06	0.01	0.01	0.02
19	0.10	−0.04	0.05	−0.04	−0.04	−0.04
20	0.13	0.00	0.06	0.00	0.00	0.00
21	0.13	−0.01	0.06	−0.01	−0.01	−0.01
22	0.13	−0.01	0.06	−0.01	−0.01	−0.01
23	0.14	0.00	0.07	0.00	0.00	0.00
24	0.13	−0.01	0.06	−0.01	−0.21	−0.21
25	0.13	−0.01	0.06	−0.01	0.00	0.00
26				0.16	0.13	0.13
27					−0.01	0.00
28					−0.01	−0.01
29					−0.01	−0.01
30					−0.01	−0.01
31					0.00	0.00
32					0.00	0.00
33						0.16

RESULTS AND DISCUSSION

Benzylideneaniline and Salicylideneaniline

A number of minimized relative orientations of very similar energy exist for BA and SA, (Table VI). Among the lowest in energy is the one found in the crystal structure of BA.

Due to the small energy differences it seems likely that both BA and SA may adopt several different packing structures depending upon the environment in each particular case.

TABLE VI

Intermolecular energies and orientations in pairs of molecules of BA, SA, MMBA and MMSA

Compound		D1	D2	D3	D	A1	A2	A3	E	rem.
BA1	(AM1)	4.3	4.0	4.0	4.0	21.6	13.7	20.8	−7.96	HH
BA2	(AM1)	4.3	3.9	3.9	3.9	14.1	7.6	35.2	−7.66	HT
BA3	(AM1)	4.2	4.8	4.4	4.4	16.3	28.4	18.0	−8.60	HH
BA4	(AM1)	4.3	4.5	3.9	3.9	37.5	14.5	44.5	−7.46	HT
BA1	(CNDO)	3.2	3.3	3.2	3.2	4.0	4.2	2.9	−11.34	HH
BA2	(CNDO)	3.3	3.3	3.2	3.2	3.0	7.0	25.0	−11.26	HT
BA3	(CNDO)	3.3	3.3	3.3	3.3	2.3	9.7	0.8	−10.86	HH
BA4	(CNDO)	3.3	3.3	3.3	3.2	7.9	7.7	25.5	−11.09	HT
BA1	(STO)	3.3	3.3	3.3	3.3	4.0	3.6	3.1	−10.17	HH
BA2	(STO)	3.3	3.4	3.2	3.2	4.7	14.0	24.4	−10.47	HT
BA3	(STO)	3.2	3.5	3.3	3.3	0.7	12.6	1.4	−9.92	HH
BA4	(STO)	3.4	3.3	3.3	3.3	8.6	5.8	26.0	−9.78	HT
SA1	(CNDO)	3.3	3.3	3.2	3.2	3.6	4.3	3.0	−12.52	HH
SA2	(CNDO)	3.4	3.3	3.3	3.3	3.3	5.7	27.4	−12.42	HT
SA3	(CNDO)	3.3	3.3	3.3	3.3	1.9	10.0	1.4	−12.49	HH
SA4	(CNDO)	3.3	3.3	3.3	3.3	5.9	6.2	27.8	−12.51	HT
MMBA1	(CNDO)	3.3	3.5	3.2	3.2	4.9	9.2	3.0	−13.59	HH
MMBA2	(CNDO)	3.3	3.5	3.1	3.1	8.1	8.8	24.2	−12.95	HT
MMBA3	(CNDO)	3.3	3.3	3.3	3.3	3.2	8.9	2.0	−14.16	HH
MMBA4	(CNDO)	3.3	3.3	3.3	3.3	7.9	7.7	25.5	−14.42	HT
MMSA1	(CNDO)	3.7	3.8	3.7	3.7	5.9	5.6	5.7	−12.97	HH
MMSA2	(CNDO)	3.6	3.5	3.3	3.3	5.9	6.3	28.6	−14.44	HT
MMSA3	(CNDO)	3.3	3.2	3.3	3.2	2.4	9.2	2.2	−15.90	HH
MMSA4	(CNDO)	3.3	3.3	3.3	3.3	6.2	6.2	27.3	−15.70	HT

D1 and D2 = Distance between close lying phenyl rings (in Å).
D3 = Distance between the imine groups (in Å).
D = Mean distance between the molecules (in Å).
A1 and A2 = Angles between close lying phenyl rings (in degrees).
A3 = Angle between the imine groups (in degrees).
E = Interaction energy (in kcal/mol).
HH = The main direction of orientation of the two molecules is "Head-to-Head."
HT = The main direction of orientation of the two molecules is "Head-to-Tail."

The pairs of molecules are relatively planar to each other in all the intermolecular orientations of the two compounds. Both the "head-to-head" (BA1, BA3, SA1, SA3) and "head-to-tail" orientations (BA2, BA4, SA2, SA4) have angles between close lying phenyl groups which are less than 10°. The angles between the imine groups are considerably larger in the latter cases (ca 25°) compared with the former (0.8–3.1°). The average interatomic distances are close to 3.3 Å, i.e. the sum of the van der Waals radii, in each case (Table VI). The orientations are depicted in Figures 1–4. The orientations of SA, not shown, are virtually identical with the ones in BA.

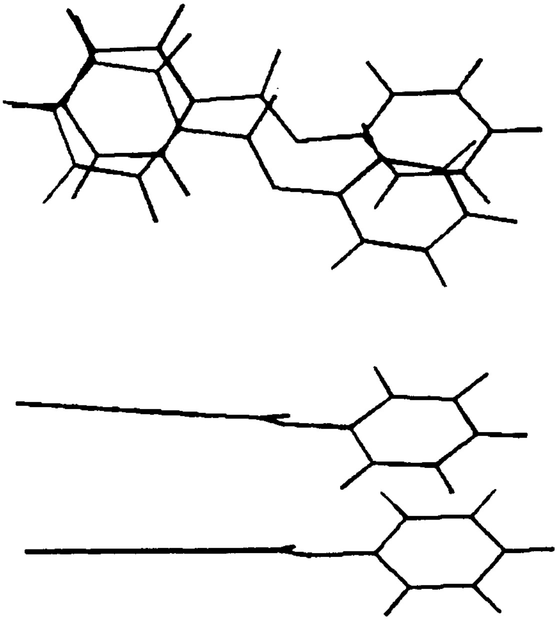


FIGURE 1a–b Intermolecular orientation of BA1 (perpendicular views).

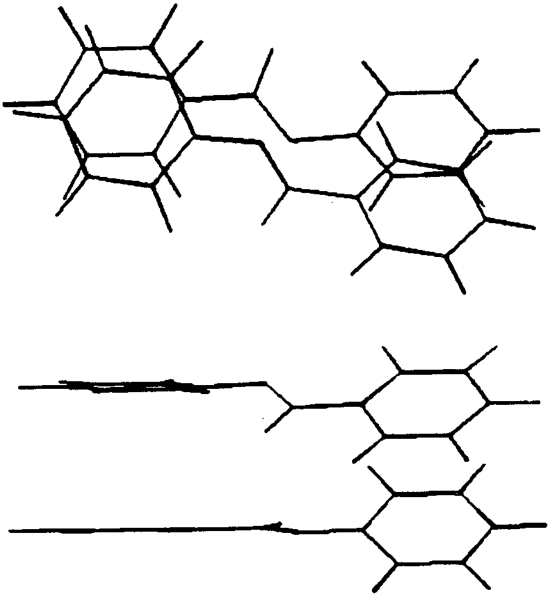


FIGURE 2a–b Intermolecular orientation of BA2 (perpendicular views).

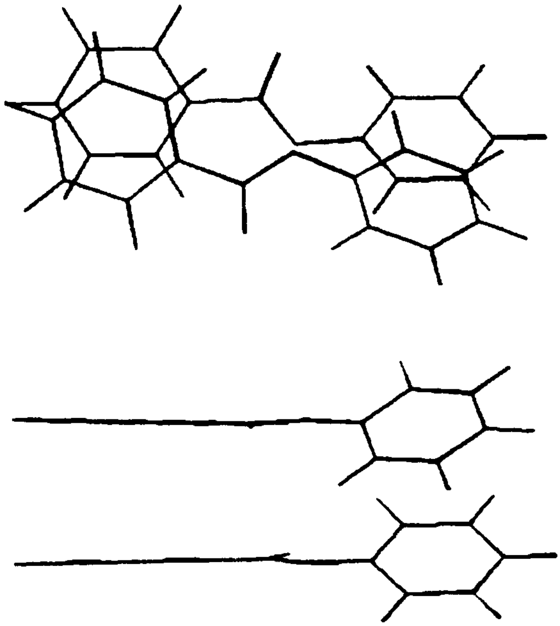


FIGURE 3a–b Intermolecular orientation of BA3 (perpendicular views).

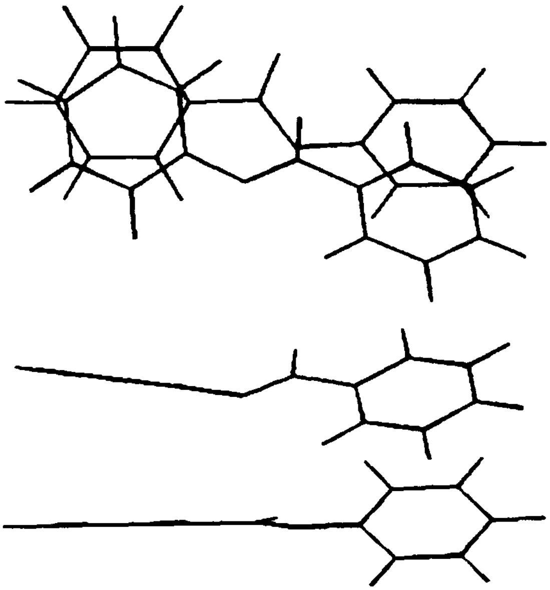


FIGURE 4a–b Intermolecular orientation of BA4 (perpendicular views).

MMBA and MMSA

Adding p-methoxy and p-methyl substituents to the C— and N—substituted phenyl ring, respectively, of BA and SA result in MMBA and MMSA. The addition of the substituents have a pronounced influence on the relative interaction energies of both MMBA and MMSA (Table VI). Two similar orientations, for both compounds, become more stabilized compaired to the other (Figures 5–6). The effect is greater in MMSA, which is possible due to intermolecular hydrogen bonding between the imine-nitrogen in one molecule and the hydroxy hydrogen of the other.

The intermolecular orientations in MMBA and MMSA are similar to the ones found for BA and SA (Table VI). The pairs of molecules are relatively planar to each other with an average distance of about 3.3 Å.

Atomic charges

The sign and size of the atomic charges are of importance when calculating the electrostatic energy and determining the relative orientations of the two molecules in a pair. In order to investigate the influence of the atomic charges, three methods (CNDO/2, AM1 and STO-3G) were used to calculate charges in BA (Table V).

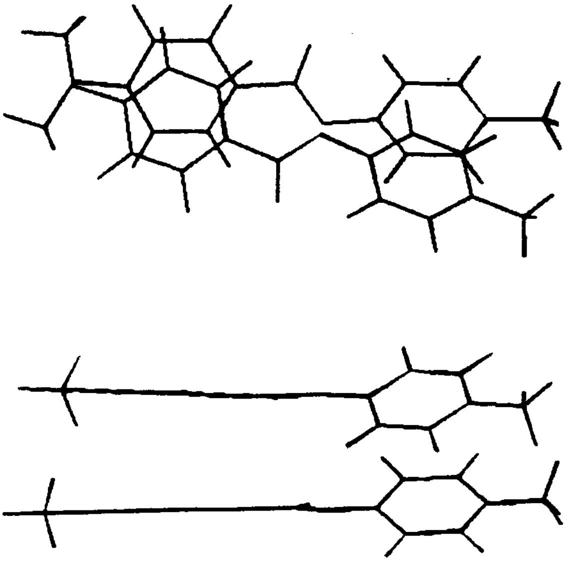


FIGURE 5a–b Intermolecular orientation of MMBA3 (perpendicular views).

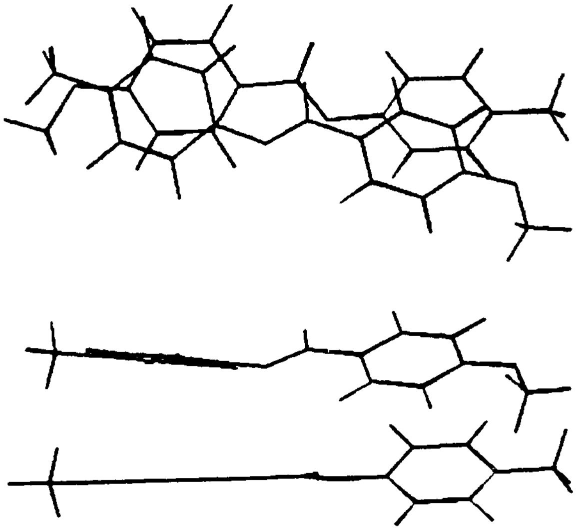


FIGURE 6a–b Intermolecular orientation of MMBA4 (perpendicular views).

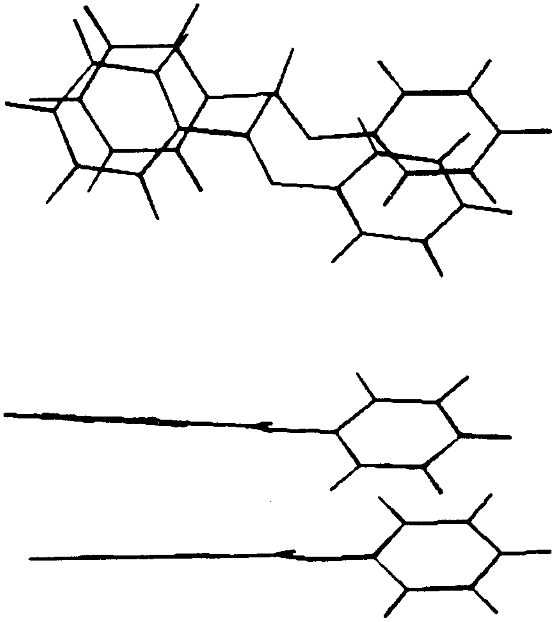


FIGURE 7a–b Intermolecular orientation of BA1 (STO-3G, perpendicular views).

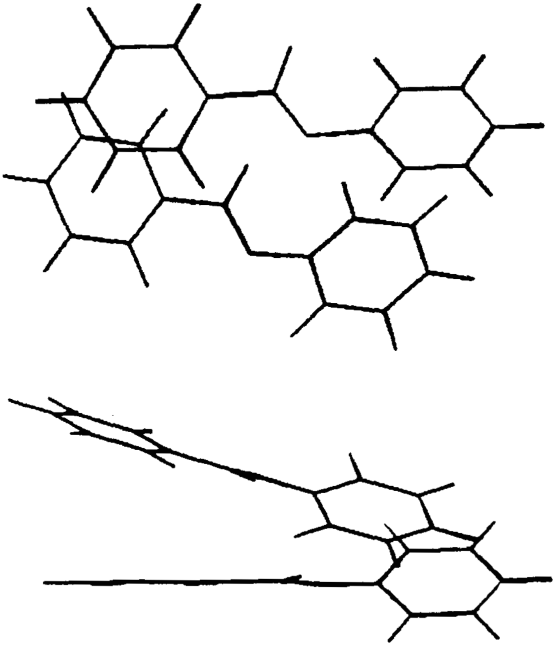


FIGURE 8a-b Intermolecular orientation of BA1 (AM1, perpendicular views).

The calculated orientations are close using CNDO/2 (Figure 1) and *ab initio* (STO-3G) (Figure 7) charges while the ordering predicted with AM1 charges (Figure 8) clearly deviates.

On average, the molecules are 0.7 Å further apart from each other in the latter case compared with the two former. Angles between close lying phenyl rings, and between the two imine moieties, are also different when using the AM1 charges compared with the ones obtained using CNDO/2 and STO-3G charges. As a result of the larger interatomic distances in the first case, the interaction energies are lower.

CONCLUSIONS

Pairs of molecules of benzylideneaniline and salicylideneaniline may adopt a number of different orientations, which are close in energy. MMBA and MMSA have two orientations, which are considerably more stable than the rest. One is a "head-to-head" ordering and the other a "head-to-tail."

Minimizations for benzylideneaniline based on charges obtained from CNDO/2 and *ab initio* (STO-3G) calculations result in virtually identical orientations, while calculations using charges predicted by AM1 give quite different orderings.

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