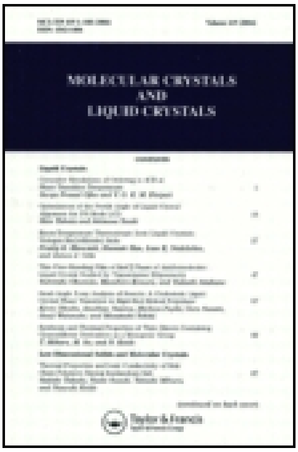

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Theoretical Investigation of Benzylideneaniline and Salicylideneanile: An AM1 Study

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Theoretical Investigation of Benzylideneaniline and Salicylideneaniline: An AM1 Study

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The conformations of benzylideneaniline and two tautomers of salicylideneaniline have been calculated using the AM1 method. The calculated geometries agree favorably with those derived from other structure determinations. The dihedral angles of the C- and N-substituted phenyl rings in benzylideneaniline are 33.9° and 6.0°, respectively. The corresponding dihedral angles in salicylideneaniline are 33.3° and 2.7°. Rotational energy barriers of the phenyl rings in benzylideneaniline appear to be underestimated by the AM1 approach by a factor of approximately 2.

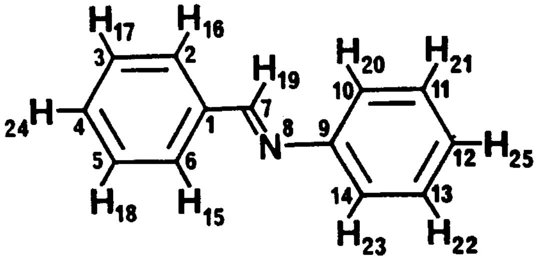
Keywords: conformational analysis, AM1, benzylideneaniline, salicylideneaniline

INTRODUCTION

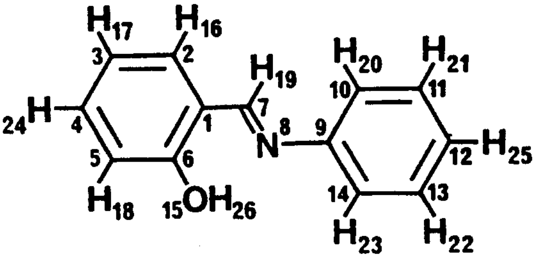
Benzylideneaniline (BA) and salicylideneaniline (SA) are important substructures in mesogenic compounds.[1–3] BA and SA represent the "polarizable core" of Schiff bases.[3]

A small number of theoretical investigations of BA and SA have been reported. Most of these concern the UV spectra of BA and various substituted derivatives.[4–9] The X-ray structures of both BA[10–13] and SA[14] have been published as well as a PES study of the former compound.[7]

In this article we describe the calculation of the geometries of BA



BA



SA

and SA and the barriers to internal rotation of the phenyl rings in the former compound, by the AM1 method.

METHOD OF CALCULATION

All calculations were carried out with complete geometry optimization, except for the transition state structures of BA, where the dihedral angle between the imine moiety and the C- and N-substituted phenyl ring was fixed at 90°.

The AM1 calculations were performed with the AMPAC program.[15–17] Chem-X was used to generate input structures and for molecular modelling.[18]

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

RESULT AND DISCUSSION

The calculated geometries of the common sub-structure of BA and SA are very similar. Bond lengths and most of the bond angles are virtually identical (Tables II–IV). A small difference in bond angle between BA and SA can be seen in the phenyl substituted ring by an hydroxy group in the latter compound. The bond angle C7-C1-C6 is a little smaller in BA (122.4°) than in SA (125.1°). The planarity of both compounds is also similar. The N-substituted phenyl ring is twisted out of the plane of the imine moiety, in both BA (33.9°) and SA (33.3°) whilst the angle of twist of the C-substituted phenyl ring is somewhat smaller in the latter compound (2.7°) compared with the former (6.0°). This is probably due to the intramolecular hydrogen-bond formed between the hydrogen of the hydroxy group and the imine nitrogen in SA.

How do these geometries compare with the structure determined by X-ray diffraction and predicted by other theoretical calculations? As can be seen from Table I, the AM1 calculations agree favorably with other types of structure elucidations. The dihedral angle of the C-substituted phenyl ring is a little smaller than previously found. However, the angle is close to values found by other theoretical calculations[4] and the PES study[7] on BA.

SA may also exist as a quinonoid tautomer (SA2) which is predicted by AM1 to be 4.3 kcal/mol less stable than SA. The geometry of SA2 is also somewhat different. The bond lengths, particularly towards the C-substituted end, of the imine moiety have changed (Table IV).

TABLE I

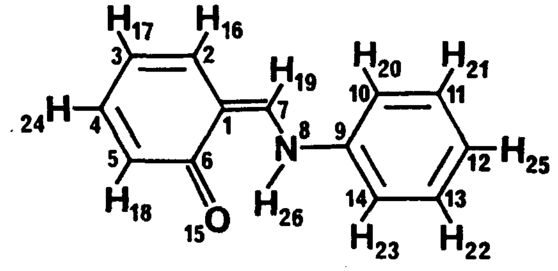
Selected molecular parameters of BA and SA

		BA					SA	SA2
		X-ray[11]	X-ray[13]	PCILO[4]	PE[7]	AM1	AM1	AM1
Bond lengths	1–7	1.496	1.440	1.455		1.469	1.465	1.386
	7–8	1.237	1.284	1.307		1.292	1.292	1.355
	8–9	1.460	1.432	1.412		1.413	1.411	1.407
Bond angles	1–7–8	122.7	125.0	122.7		123.1	123.9	125.9
	6–1–7	120.1	120.0	120.0		122.4	125.1	123.4
	7–8–9	119.9	115.0	120.0		121.2	121.7	124.6
	8–9–10	123.7	122.7	123.0		123.2	123.3	122.3
Dihedral angles	D1	55	52	36	36	34	33	21
	D2	10	0	0		6	3	−1

D1 = The dihedral angle between the N-substituted phenyl ring and the imine moiety.

D2 = The dihedral angle between the C-substituted phenyl ring and the imine moiety.

Bond lengths in Å and angles in degrees.



SA2

The carbon-carbon and the carbon-nitrogen bond have become virtually equal in length. The compound is also more planar (Table I). This is not surprising since the imine carbon bonded to the phenyl ring should, formally, assume more double bond character, whilst the C-N bond should become more single bond like, thus promoting

TABLE II

Geometry of BA

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 III

Geometry of SA

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.

planarity of the C-substituted phenyl ring. The bond lengths of the latter are also affected. The "phenyl" ring exhibits alternation of bond lengths with typical carbon-carbon single and double bonds in those positions which would be expected for the formal tautomerization process. The N-substituted ring is not, however, affected.

What about the barriers to internal rotation of the phenyl rings in BA? AM1 predicts the barrier to rotation of the C- and N-substituted phenyl rings to be 7.8 and 4.4 kJ/mol, respectively. These values seem, however, to be somewhat small, bearing in mind the fact that the corresponding barrier in *trans*-stilbene has been measured[19] and calculated (ab initio, 6-31G[20]) as 13.7 and 13.2 kJ/mol, respectively. The calculated AM1 barrier for *trans*-stilbene is 6.9 kJ/mol.[21] A value of 21.7 kJ/mol for the barrier to rotation of the N-substituted phenyl ring in BA has been predicted using the CNDO/2 method.[9] With

TABLE IV

Geometry of SA2

Atom i	Bond length (i-j)	Bond angle (i-j-k)	Dihedral angle (i-j-k-l)	j	k	l
1						
2	1.441			1		
3	1.354	121.92		2	1	
4	1.437	120.14	−0.12	3	2	1
5	1.350	120.91	−0.16	4	3	2
6	1.464	118.58	0.50	1	2	3
7	1.385	118.05	−179.63	1	2	3
8	1.354	125.87	−179.61	7	1	2
9	1.407	124.30	179.13	8	7	1
10	1.410	122.46	23.09	9	8	7
11	1.392	120.02	179.62	10	9	8
12	1.393	120.76	−0.75	11	10	9
13	1.394	119.56	0.03	12	11	10
14	1.415	118.64	−158.21	9	8	7
15	1.251	122.81	179.27	6	1	2
16	1.102	117.54	−179.56	2	1	6
17	1.098	121.51	179.88	3	2	1
18	1.100	122.28	180.02	5	4	3
19	1.112	118.24	−0.48	7	1	2
20	1.099	121.00	0.32	10	9	8
21	1.100	119.27	179.69	11	10	9
22	1.100	119.93	−179.73	13	12	11
23	1.101	120.38	0.66	14	9	8
24	1.101	117.84	179.84	4	3	2
25	1.099	120.26	−179.81	12	11	10
26	1.006	118.69	3.53	8	7	1

Bond lengths in Å and angles in degrees.

these values in mind, a value between 10–15 kJ/mol for the barriers to internal rotation in BA seems somewhat more realistic. Rotational barriers in SA have not been evaluated due to inadequate handling of intra-molecular hydrogen bonding by AM1.[21]

CONCLUSIONS

AM1 predicts reasonable geometries for both benzylideneaniline and salicylideneaniline. The energy barriers to internal rotation of the phenyl rings are, however, underestimated by this approach by a factor of about 2.

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