HETEROCYCLES, Vol. 29, No. 1, 1989

TAUTOMERISM OF BIS(2-BENZOTHIAZOLYL)ARYLMETHANES.

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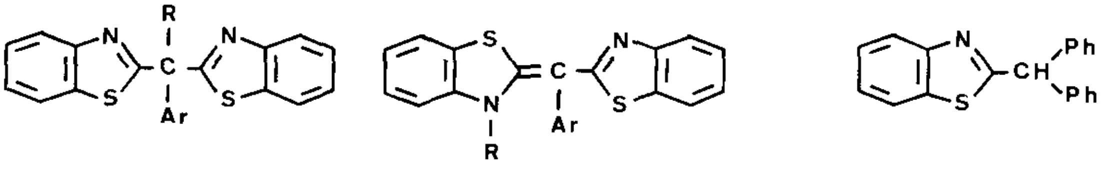
Abstract- Tautomerism of some bis(2-benzothiazolyl)methanes has been studied by ^1H nuclear magnetic resonance, ultraviolet, and infrared spectroscopies using C-methyl and N-methyl derivatives as model compounds of the "CH" and "NH" fixed forms. X-Ray diffraction analysis of compound 6 shows that it corresponds to the Z-sE isomer b_2. The presence of two 2-benzothiazolyl groups is necessary for the "NH" tautomer to be stable.

The tautomerism of heteroaromatic compounds has been so thoroughly studied that few problems remain unexplored.[1] One of them is the tautomerism of bis(heteroaryl)methanes, where only the case of bis-pyridyl, -quinolyl, and -benzoquinolylmethanes has received considerable attention, but more than twenty years ago.[2] We wish to report our results on the related bis(2-benzothiazolyl)methanes, a system of considerable interest both for its complexing abilities and for the derived cyanine dyes. Two tautomeric forms: CH (a) and NH (b) can be proposed for monosubstituted derivatives in the methane carbon atom of bis(2-benzothiazolyl)methanes, which can be considered as heterocyclic analogues of β-diketones. The tautomeric equilibrium in these series was first studied for the most simple derivatives: bis(2-benzothiazolyl)methane and 1,1-bis(2-benzothiazolyl)ethane.[3] We study here aryl- and heteroarylbis(2-benzothiazolyl)methanes 1-4 (Figure 1). As it occurred with the unsubstituted and C-methyl substituted bis(2-benzothiazolyl)methanes, the superimposition of CH/NH tautomerism and air-oxidation to carbinols,[4] precludes the usual treatment of tautomeric equilibria. Compounds 5 (type a structure, with Ar= Ph and R= CH_3), 6 (type b structure, with

Ar= Ph and R= CH_3), and 7 have also been included as reference models.



a   b   7

1 Ar= Ph, R= H

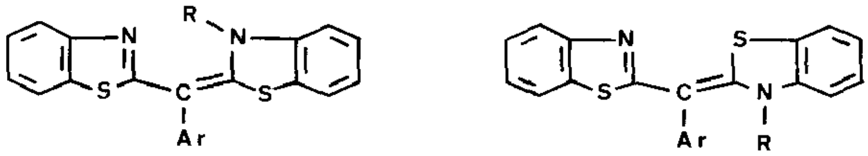
2 Ar= p-$NO_2C_6H_4$, R= H

3 Ar= 2-pyridyl, R= H

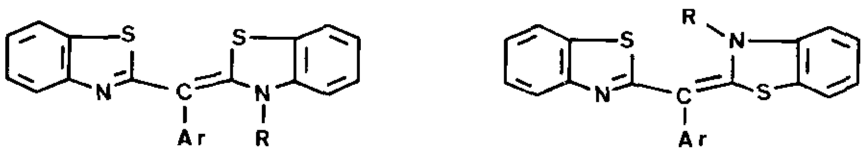
4 Ar= 2-benzothiazolyl, R= H

Figure 1

It must be remarked that the NH (b) forms can give place to three different isomers: E-sE,* Z-sZ, and Z-sE (or E-sZ)[3] (Figure 2, R= H). Other structures which could be possible for the more complicated case of compounds 3 and 4, have not been depicted.



b_1, E-sE b_2, Z-sE



b_3, Z-sZ b_4, E-sZ

Figure 2

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* The old nomenclature s-cis/s-trans (single cis/single trans) for describing single bonds with double bond character has been replaced by the less ambiguous single E/single Z (sE/sZ) notation.[5]

The structural analysis has been undertaken by ^{1}H nmr, ir, and uv spectroscopies and X-ray diffraction analysis of compound 6.

X-Ray study of compound 6.

Figure 3 shows a view of molecule 6 and the numbering for the crystallographic study. Bond lengths, and valence and torsion angles can be found in Table 1.

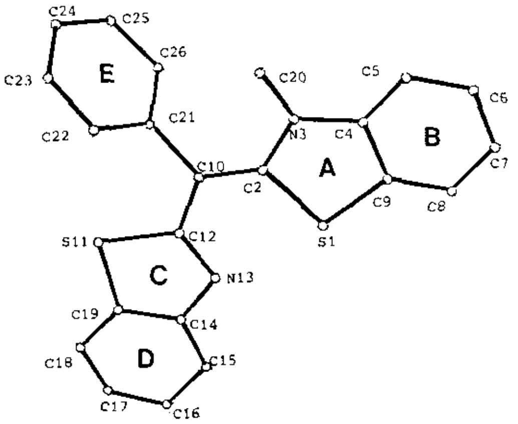

Figure 3.- A view of molecule 6 with atomic numbering.

The molecular rings are planar (mean torsion angles of the five rings A, B, C, D, and E are: 2.7(8), 1.5(6), 2.6(6), 3.0(7), and 2.7(8)° respectively) and the two benzothiazolyl groups are approximately in a plane (the dihedral angle between them is 2.2(1)°). Similarly to the results[3] found for the simpler analogue 8, this structure corresponds to a Z-sE or b_2 isomer. The mean torsion angle about the C10-C21 bond is 113.5(6)°. Since there are not significative differences between compounds 6 and 8, it must be concluded that the C-phenyl substituent exerts no influence on the conjugation of the bis(2-benzothiazolyl)methane system.

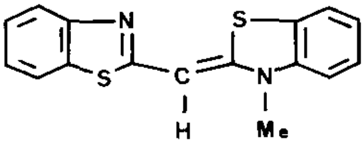

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Figure 4

Table 1.- Bond lengths (Å), bond angles (°), and some torsion angles (°) of compound 6.

Bond lengths (Å)

S1 - C2	1.778(7)	S1 - C9	1.757(6)
C2 - N3	1.410(8)	C2 - C10	1.354(7)
N3 - C4	1.405(5)	N3 - C20	1.456(6)
C4 - C5	1.362(7)	C4 - C9	1.382(7)
C5 - C6	1.370(5)	C6 - C7	1.358(9)
C7 - C8	1.382(9)	C8 - C9	1.404(6)
C10 - C12	1.403(8)	C10 - C21	1.488(8)
S11 - C12	1.780(5)	S11 - C19	1.727(5)
C12 - N13	1.307(5)	N13 - C14	1.433(8)
C14 - C15	1.376(8)	C14 - C19	1.392(7)
C15 - C16	1.400(6)	C16 - C17	1.339(5)
C17 - C18	1.365(7)	C18 - C19	1.402(6)
C21 - C22	1.348(6)	C21 - C26	1.423(9)
C22 - C23	1.312(8)	C23 - C24	1.427(7)
C24 - C25	1.343(6)	C25 - C26	1.389(8)

Bond angles (°)

C2 - S1 - C9	92.2(3)	S1 - C2 - C10	124.5(4)
S1 - C2 - N3	108.0(4)	N3 - C2 - C10	127.5(5)
C2 - N3 - C20	123.9(4)	C2 - N3 - C4	115.7(4)
C4 - N3 - C20	119.0(3)	N3 - C4 - C9	112.6(3)
N3 - C4 - C5	126.7(4)	C5 - C4 - C9	120.8(3)
C4 - C5 - C6	116.5(4)	C5 - C6 - C7	125.6(4)
C6 - C7 - C8	117.6(5)	C7 - C8 - C9	118.5(4)
C4 - C9 - C8	120.8(4)	S1 - C9 - C8	127.6(3)
S1 - C9 - C4	111.5(3)	C2 - C10 - C21	124.2(4)
C2 - C10 - C12	118.5(4)	C12 - C10 - C21	117.0(3)
C12 - S11 - C19	90.1(3)	C10 - C12 - S11	120.0(3)
S11 - C12 - N13	113.0(3)	C10 - C12 - N13	126.8(4)
C12 - N13 - C14	112.8(4)	N13 - C14 - C19	112.8(4)
N13 - C14 - C15	126.4(4)	C15 - C14 - C19	120.2(3)
C14 - C15 - C16	117.7(4)	C15 - C16 - C17	122.1(5)
C16 - C17 - C18	121.1(4)	C17 - C18 - C19	118.7(4)
C14 - C19 - C18	120.0(4)	S11 - C19 - C18	128.9(4)
S11 - C19 - C14	111.1(3)	C10 - C21 - C26	118.7(3)
C10 - C21 - C22	123.0(5)	C22 - C21 - C26	118.3(5)
C21 - C22 - C23	122.4(5)	C22 - C23 - C24	121.0(4)
C23 - C24 - C25	118.1(4)	C24 - C25 - C26	120.8(4)
C21 - C26 - C25	119.2(3)		

Some torsion angles (°)

S1 -C2 -C10-C12	6.5(8)	S1 -C2 -C10-C21	-166.3(4)
S1 -C2 -N3 -C20	-163.8(4)	N3 -C2 -C10-C12	-175.3(5)
N3 -C2 -C10-C21	11.9(9)	N3 -C4 -C9 -S1	1.3(5)
C2 -C10-C21-C22	-117.8(6)	C2 -C10-C21-C26	63.6(7)
C2 -C10-C12-N13	-6.7(7)	C2 -C10-C12-S11	178.9(4)
C12-C10-C21-C22	69.4(7)	C12-C10-C21-C26	-109.2(5)
N13-C14-C19-S11	-4.0(6)		

^{1}H Nuclear magnetic resonance.

In spite of the great complexity, even at 300 MHz, of the ^{1}H nmr spectra of the compounds studied, the connectivities between protons and precise chemical shifts and coupling constants have been established by the combined use of bidimensional techniques and theoretical analysis of the spectra. The main problem was to distinguish between H4 and H7 benzothiazole protons. The two assignment criteria followed in our previous work[3] are also valid here (δH4 > δH7 in $CDCl_3$ solutions and δH7 > δH4 in DMSO-d_6 solutions, and $J_{45} > J_{67}$).

The chemical shifts and coupling constant values in $CDCl_3$ and DMSO-d_6 are in Tables 2 and 3. We will first analyse the fixed a and b forms of model compounds 5 and 6.

Compound 5 exhibited the expected ABCD system which was interpreted following the criteria mentioned above. Compound 6 showed two ABCD systems. The chemical shifts of the system formed by H4'-H7' protons (specially the H4') appeared at higher field than those of the ABCD system formed by the H4-H7 protons. The first mentioned system was assigned to the benzothiazoline ring.

The CH forms of compounds 1-4 were characterized by the CH chemical shift at δ = 6.3-6.6 ppm in $CDCl_3$ and 6.7-7.1 ppm in DMSO-d_6, while the NH tautomers gave broad signals (specially in DMSO-d_6), and higher chemical shifts for H4-H7 protons. Autotropic prototropy interconverts isomers b_2 (Z-sE) and b_4 (E-sZ) ($b_2 \rightleftarrows b_4$) and both isomers give an averaged ABCD system for the benzothiazole protons. Since b_1 isomers also give an averaged ABCD system, and the signal corresponding to the NH resonance was not observed in most cases, this method is not suitable for a general attribution to different b isomers.

Although the rapid oxidation of the NH forms[4] made impossible to determine any precise tautomeric constant, the changes observed in the relative populations of NH/CH forms in $CDCl_3$ and DMSO-d_6 were as follows. The spectrum of a freshly prepared $CDCl_3$ solution of 1, in which the NH tautomer was the predominant form, changed to a mixture of tautomers with relative populations NH/CH: 34%/66% after about ten minutes, and 23%/77% after a week, while a freshly prepared DMSO-d_6 solution showed a relative population NH/CH of 47%/53%. The different populations observed in both solvents are in accordance with the results discussed in our previous study,[3] indicating that the greater polarity of the DMSO-d_6 would stabilize the CH forms.

The spectrum of compound 2 in $CDCl_3$ solution corresponds to the NH tautomer, and the only observed change with time was its oxidation to the corresponding carbinol.[4] The spectrum in DMSO-d_6 solution was not very good due to the low solubility of 2 in this solvent, and only the CH tautomeric form could be detected, showing again the influence of the solvent polarity in the tautomeric equilibrium.

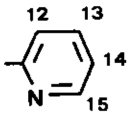
Table 2.- ^{1}H Nmr data in $CDCl_3$ and DMSO-d_6 of the CH forms of compounds 1-5 and 7 (300 MHz)

δ ppm

	$CDCl_3$					DMSO-d_6				
	1	3	4	5	7	1	2	3	5	7
H4	8.039	8.045	7.964	8.063	8.018	8.011	8.013	7.995	8.024	7.970
H5	7.461	7.458	7.364	7.473	7.459	7.525	7.531	7.513	7.529	7.498
H6	7.367	7.367	7.270	7.373	7.342	7.455	7.477	7.445	7.458	7.419
H7	7.855	7.849	7.720	7.829	7.807	8.093	8.130	8.080	8.078	8.042
CH	6.352	6.562	6.618	---	5.946	6.764	7.076	6.836	---	6.118
Ar	7.3-7.8	*a*	---	7.34-7.31	7.25-7.31	7.3-7.7.	7.790 8.353	*b*	7.40-7.31	7.28-7.38
CH_3	---	---	----	2.573	---	---	---	---	2.491	---

J(Hz)

	$CDCl_3$					DMSO-d_6				
	1	3[c]	4	5	7	1	2	3[d]	5	7
J_{45}	8.28	8.15	8.25	8.26	8.12	8.33	8.19	8.25	8.25	8.20
J_{46}	1.13	1.10	1.12	1.11	1.22	1.25	1.25	1.11	1.14	1.19
J_{47}	0.66	0.57	0.61	0.62	0.65	0.61	0.63	0.61	0.64	0.73
J_{56}	7.21	7.26	7.25	7.25	7.20	7.06	7.33	7.16	7.27	7.24
J_{57}	1.22	1.19	1.20	1.20	1.31	1.09	1.23	1.21	1.24	1.22
J_{67}	8.08	8.04	8.09	8.06	7.91	7.97	8.12	8.00	8.07	7.98



[a] δ (ppm): H12, 7.609; H13, 7.726; H14, 7.275; H15, 8.703. [b] δ (ppm): H12, 7.764; H13, 7.908; H14, 7.430; H15, 8.671. [c] $J_{12,13}$, 7.70; $J_{12,14}$, 1.15; $J_{12,15}$, 0.80; $J_{13,14}$, 7.58; $J_{13,15}$, 1.76; $J_{14,15}$, 4.94 Hz. [d] $J_{12,13}$, 7.67; $J_{12,14}$, 1.03; $J_{12,15}$, 0.75; $J_{13,14}$, 7.34; $J_{13,15}$, 1.81; $J_{14,15}$, 4.90 Hz.

Table 3.- ^{1}H Nmr data in CDCl$_3$ and DMSO-d$_6$ of the NH forms of compounds 1-4 and 6 (300 MHz).

	δ ppm									
	CDCl$_3$						DMSO-d$_6$			
	1	2	3 ^{a}	4	4b$_1$	6	1 ^{a}	3 ^{a}	4b$_1$	6
H4	7.537	7.596	7.6	7.612	8.037	7.942	7.7	7.8	8.02	7.827
H5	7.317	7.378	7.4	7.352	7.491	7.387	7.5	7.4	7.56	7.406
H6	7.084	7.162	7.2	7.109	7.321	7.168	7.1	7.2	7.38	7.205
H7	7.463	7.534	7.6	7.485	7.900	7.633	7.8	7.8	8.09	7.799
H4'					7.808	6.873				7.173
H5'					7.468	7.262				7.333
H6'					7.297	7.099				7.150
H7'					7.736	7.532				7.763
NH	b	b	b	b	15.71	---			15.20	---
CH$_3$	---	---	---	---	---	2.999	---	---	---	3.359
Ar	7.3-7.8	7.790 8.353				7.4-7.5				7.4-7.6

	J(Hz)					
	CDCl$_3$					DMSO-d$_6$
	1	2	4	4b$_1$	6	6
J_{45}	8.10	8.11	8.10	8.22	8.16	8.04
J_{46}	1.15	1.13	1.13	1.10	1.64	1.15
J_{47}	0.65	0.64	0.52	0.67	0.65	0.70
J_{56}	7.34	7.32	7.32	7.12	7.25	7.25
J_{57}	1.21	1.18	1.17	1.39	1.45	1.30
J_{67}	7.86	7.88	7.87	7.90	7.90	7.95
$J_{4'5'}$				8.20	8.16	8.42
$J_{4'6'}$				1.03	1.64	1.26
$J_{4'7'}$				0.67	0.60	0.70
$J_{5'6'}$				7.14	7.24	7.65
$J_{5'7'}$				1.05	1.42	1.33
$J_{6'7'}$				8.00	7.87	7.76
$J_{4'CH_3}$					0.3	b

[a] Broad signals, only approximate values. [b] Not observable.

The $CDCl_3$ solution of compound 3 revealed a tautomeric mixture ratio NH/CH of 56%/44%, while the DMSO-d_6 solution showed the NH forms to be predominant (NH/CH: 61%/39%). The existence in this compound of the pyridine group, that must give place to new NH tautomeric forms, introduces a new structural factor which can not be easily interpreted.

We have obtained three solid samples for compound 4 with different spectroscopic properties. One of them corresponded, in $CDCl_3$ solution, to the CH tautomer exclusively (4a). The $CDCl_3$ solution of other sample, greenish-yellow in colour, showed two ABCD systems in 2:1 ratio together with a very low field signal at 15.7 ppm. These data are in agreement with the $4b_1$ isomer (Figure 5).

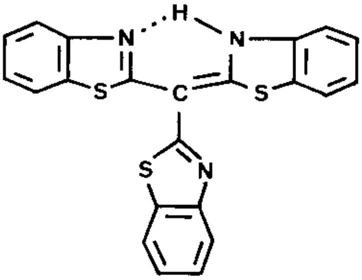


Figure 5

The two benzothiazole rings which are bonded through the intramolecular NH•••N bond would give place to an averaged ABCD system, while the nonbonded benzothiazole ring would give a different ABCD system. The chemical shift of the NH signal (which was not visible in the previous NH forms studied) is in accordance with those described for δ OH and δNH values of other intramolecular bonded dicarbonyl compounds[6] and bis(2-pyridyl)methane derivatives.[2] The DMSO-d_6 spectrum of this tautomer showed very broad signals precluding a precise determination of the spectral parameters.

The third solid sample is an approximate 1:1 mixture of CH and NH tautomers. The presence of a single ABCD system found for the NH tautomer, indicated a symmetrical structure assigned to $4b_2 \rightleftarrows 4b_4$, in which the third benzothiazole group is also implied.

Finally, the spectra of compound 7 in $CDCl_3$ and DMSO-d_6 solutions, corresponded to the CH tautomer exclusively and showed no change with time.

Infrared study.

Table 4 shows the characteristic ir bands of compounds 1-7 including some Raman data. The ir spectra of compounds 5 and 7 in the solid state showed the three characteristic benzothiazole bands[3] and no significative changes took place in $CDCl_3$ solution. The same pattern was observed in the Raman spectra in the solid state. On the contrary, the ir spectra of compound 6 in the solid and in $CDCl_3$ solution were characterized by a very strong band at ca. 1530 cm^{-1}, assigned to coupled vibrations in the planar N=C-C=C system, and a weak band at ca. 1580 cm^{-1} assigned to the benzothiazole I band. The third expected weak benzothiazole band at ca. 1555 cm^{-1} appeared overlapped by the first mentioned strong band. The above data are in accordance to those previously found for the CH and NH models respectively.[3]

The ir data of compound 1 in the solid state pointed out to an NH form (b) showing the strong absorption band assigned to the N=C-C=C system at 1560 cm^{-1}. The absorption pattern was also similar to that found for the NH forms studied before.[3] The benzothiazole I band appeared in this compound at 1595 cm^{-1} and, as it could be expected,[3] both bands were weak in the Raman spectrum of the solid. In $CDCl_3$ solution, the intensity of the band at 1565 cm^{-1} (N=C-C=C system) decreased with time. The presence of the CH form (detected by ^1H nmr), could not be easily distinguished from the oxidation product, evidenced by the appearance of a broad absorption at about 3420 cm^{-1} attributed to νOH stretching. In DMSO-d_6, the change to the CH form (and/or to the carbinol) took place quicker than in chloroform solution. It must be remarked that the ν NH band of the NH tautomer could not be detected either in the solid nor in $CHCl_3$ solution. However, in dilute CCl_4 solution a broad weak absorption centered at about 3050 cm^{-1} could be observed, this absorption being attributed to the presence of an intramolecularly bonded NH···N group (b_1).

The ir spectrum of compound 2 in the solid state was similar to that of compound 1 showing the characteristic N=C-C=C absorption at 1555 cm^{-1} (very strong). The asymmetric stretching mode of the NO_2 group appeared in this compound at 1512 cm^{-1}. The same features were observed in a freshly prepared chloroform solution. As in compound 1, the intensity of the band at 1555 cm^{-1} decreased with time. Although the spectrum in CCl_4 has not been recorded due to solubility problems, we assume for this compound the b_1 structure.

The ir spectrum of compound 3 in the solid state was complicated in the 1500-1600 cm^{-1} region by the presence of the pyridine bands. As in previous cases, the strong band at 1545 cm^{-1} was assigned to the N=C-C=C coupled mode of the NH form. In $CDCl_3$ and DMSO-d_6 solutions, this band appeared at ca. 1525 cm^{-1}. The shift towards lower frequencies observed by N-deuteration (in $CDCl_3$) confirmed the assignment of this band to a complex coupled vibration of the enamine system of the NH forms. The intensity decreasing of this band compared with that found in the spectrum in KBr was attributed to an increasing of the CH tautomer already present in the solid. Moreover, the ir data showed that the NH form observed in solution is different from the original crystalline form. In CCl_4, results were similar to those of $CDCl_3$ solution although a greater proportion of the NH form was observed. The spectrum of a very dilute CCl_4 solution showed a broad complex absorption between 3400 and 2400 cm^{-1} which was attributed to the presence of intramolecular NH•••N bonding.

The three solid samples found for compound 4 gave different infrared spectra (Table 4). The KBr

Table 4.- Infrared and Raman characteristic frequencies (cm^{-1}) for compounds 1-7.

			Benzothiazole bands					
Compound	Medium	ν (N-H)	I	II	III	N=C-C=C	Other ring bands	
$1b_1$	KBr	*a*	1595m [b,c]			1560vs	1449s	1433vs
	Solid (Raman)	*a*	1583w	*a*		1558w	1450s	1434vs
	CDCl$_3$	*a*	1595m [c]			1565vs	1450s	1435vs
	CCl$_4$	3400-2500br [d]						
$2b_1$	KBr	3200-2300br	1584sh	1563sh		1555vs	1451s	1435vs
	CHCl$_3$	*a*	1584sh	1562sh		1555vs	1451s	1435s
3 [e]	KBr	*a*	1588w	1554w		1545vs	1448vs	1435vs
	Solid (Raman)	*a*	1583w	1560w		1545w	1449m	1437vs
	CDCl$_3$	*a*	~1590	1560w		1528s	1457m 1450m	1437s
	CCl$_4$	3400-2400br [d]	1595sh	1560sh		1524s	1451m	1436s
4a	KBr		1593vw	1555w	1500s		1456m	1432s
	CDCl$_3$		1595vw	1561vw	1503m		1456w-m	1433s
$4b_1$	KBr	3200-2400br	1600w 1590sh	1560w	1473vs	1518vs	1453s	1438vs
	Solid (Raman)	*a*	1585w	1560w	1473s	*a*	1454s	1434vs
	CDCl$_3$	*a*	1600w 1590sh	1560vw	1474s-vs	1519vs	1453s-vs	1438vs
	CCl$_4$	3300-2500br [d]						
$4b_4$	KBr	3200-2400br	1598w	1561sh		1555vs	1452s	1435s
	CDCl$_3$	*a*	1597w	1560sh		1554vs	1451s	1434vs
	CCl$_4$	3300-2700br [d]						
5a	KBr		1580vw	1553vw	1493s		1455m	1433s
	Solid (Raman)		1580vw	1556m	1502vs		1455w	1436m
	CDCl$_3$		1580vw	1557vw	1492m		1455w	1435m
$6b_2$	KBr		1585w 1573w	1555sh		1528vs	1457s 1448s	1435s 1419vs
	Solid (Raman)		1585w [c] 1574vw	1557vw		1522vw	1457m 1447m	1434s 1412vs
	CHCl$_3$		1588w 1574w	1558sh		1530vs	1461vs 1451s	1436s 1422vs
7a	KBr		1582vw	1555vw	1492vs		1448s	1432s
	Solid (Raman)		1586w	1555w	1496vs		1448vw	1430w-m
	CDCl$_3$		1584vw	1560vw	1492s		1455w	1442w 1436w

[a] Not detected. [b] Abreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.
[c] Possible contribution of ring ν(C=C). [d] Very dilute solution. [e] Mixture of NH and CH tautomers.

spectrum of the greenish-yellow solid form presented the strong N=C-C=C band characteristic of the NH forms at 1518 cm^{-1} and also showed another strong band at 1473 cm^{-1} which was assigned to the benzothiazole III band of the third ring. In this case, a broad absorption at 3200-2400 cm^{-1} was observed which was assigned to a NH stretching vibration. As this absorption was also observed in very dilute CCl_4 solution, it can be deduced the existence of an intramolecular NH•••N bond ($\underline{b}_1$ isomer). Results in $CDCl_3$ solution were similar and no noticeable changes were observed with time (four days). In DMSO-d_6 solution (very low solubility) the $\underline{b}_1$ form was also observed.

The spectrum of the sample characterized by ^1H nmr as 4a showed in the solid state the three characteristic benzothiazole bands of a CH form (4a). In $CDCl_3$ solution, the spectrum of this sample gradually changed to a NH form different from $\underline{4b}_1$ (see above), as it was revealed by the appearance of the enamine band at 1555 cm^{-1} and the corresponding disappearance of the benzothiazole band at 1503 cm^{-1}. This absorption pattern was similar to that observed for the third solid sample, assigned to a CH/NH mixture by ^1H nmr. It must be remarked that the spectrum of this NH form in the solid state showed a complex broad absorption at about 3200-2400 cm^{-1} which was also present in very dilute CCl_4 solution, and in this case may be assigned to intramolecular NH•••S bonding.

Ultraviolet study.

Ultraviolet absorption data of compounds 1-7 are summarized in Table 5. Methanol was the solvent of choice, although chloroform solutions were used for compounds 2, 3, and 4 due to solubility reasons. Two different absorption patterns were observed for model compounds 5 and 6. Compound 5, a fixed a form, showed absorption maxima corresponding to the benzothiazole rings. Compound 6, a fixed b form, showed, together with the mentioned benzothiazole absorption bands, a strong absorption band at 405 nm, according to the extended conjugation, and in the same way as it was observed for the b forms in the simpler derivatives previously studied.[3]

Compounds 1-4, except 4a, gave colored solutions with intense absorption bands at the λ = 390-430 nm region, similar to those found in the NH model compound 6. These solutions faded with time, specially when they were exposed to sunlight, and the final colorless solution showed no absorption in the above mentioned region, giving an absorption pattern analogous to the CH model compound 5, with absorption maxima below 300 nm. This change, which could be attributed exclusively to the tautomeric displacement of NH to CH tautomers, corresponds however, as it was deduced from different experimental data, to the oxidation to carbinol derivatives, which give similar uv absorption patterns to that expected for the CH forms.[4]

Compounds 7 and 4a showed typical absorption bands of a CH tautomer. No changes were observed with time for compound 7, in agreement with the results obtained by other techniques, while the chloroform solution of 4a showed, after 24 hours, the absorption bands of NH tautomers at 400 nm.

Table 5.- Ultraviolet data of compounds 1-7 in freshly prepared solutions.

Compound	Solvent [a]	λ (nm) (log ε)				
1	MeOH	205	268	394	414	435
		(4.74)	(4.00)	(4.15)	(4.65)	(4.87)
2	CHCl$_3$	267	392	410		
		(4.29)	(4.42)	(4.45)		
3	MeOH	218	260	400	408	426
		(4.54)	(4.22)	(4.36)	(4.44)	(4.16)
3	CHCl$_3$	263	400	417		
		(4.27)	(4.22)	(4.28)		
4a	CHCl$_3$	265	284	296		
		(4.42)	(4.11)	(3.87)		
4b$_1$	CHCl$_3$	269	363	401	418	
		(4.27)	(4.51)	(4.57)	(4.66)	
5	MeOH	203	217	256	283	294
		(4.84)	(4.80)	(4.36)	(3.91)	(3.77)
6	MeOH	203	223	265	318	405
		(4.64)	(4.45)	(4.00)	(3.70)	(4.51)
7	MeOH	203	217	255	262	279
		(4.74)	(4.61)	(4.03)	(3.98)	(3.48)

[a] The spectra in methanol and in chloroform were recorded in the ranges of 200-600 nm and 245-600 nm respectively.

Conclusions.

A summary of the circumstantial evidence concerning the tautomerism of compounds 1-4 deduced from the different spectroscopic techniques, is given in Table 6. According to that, most compounds have been obtained as solid NH tautomers. Compound 4 has also been isolated as the CH tautomer. *The greater polarity of DMSO-d$_6$ compared to CDCl$_3$ favours the breaking of the* NH$\cdots$N bonds, and the rapid transformation of NH to CH tautomers. Regarding the structure-tautomerism relationship, all compounds studied that have at least two benzothiazole groups are capable of tautomerism. Introduction of substituents at the methane carbon atom stabilizes the NH tautomer which is the form in the solid state although, in some cases, both tautomers have been isolated.

Table 6.- Summary of spectroscopic data of compounds 1-4 and 7.

	Solid	Solution [a]			
	ir	ir	uv	^{1}H nmr	
Compound	(KBr)	($CDCl_3/CCl_4$)	($CHCl_3$/MeOH)	($CDCl_3$)	(DMSO-d_6)
1	1b	$1b_1$	1b	1b	47% 1b/53% 1a
2	2b	2b	2b	2b	2a
3	3a+3b	3a+3b	3b [b]	56% 3b/44% 3a	61% 3b/39% 3a
4	4a	4a	4a	4a	[c]
	$4b_1$	$4b_1$	4b	$4b_1$	4b
	4a+$4b_4$	4a+$4b_4$	[c]	50% 4a/50% $4b_4$	[c]
7	7a	7a	7a	7a	7a

[a] Freshly prepared solutions. [b] The presumable presence of the a tautomers is not easily evidenced since benzothiazole bands are also present in the NH tautomer. [c] Not registered.

EXPERIMENTAL

Crystallographic analysis of compound 6.

A crystal of about 0.1x0.1x0.3 mm was mounted along the long axis. The cell dimensions were refined from 39 general reflections with the Bragg angle Θ_{max} 20° on an Enraf-Nonius CAD 4 diffractometer. Crystal data were: $C_{22}H_{16}N_2S_2$, monoclinic, $P2_1/n$; a= 11.805(3), b= 8.896(3), c= 17.454(4) Å, β= 100.13(3)°, V= 1804.4(9) $Å^3$, z= 4, D_c= 1.3712 g/cm^3. MoK$_\alpha$, λ = 0.7107 Å, (graphite monochromator), μ= 2.896 cm^{-1}, F(000)= 776.

A total of 3916 independent reflections was measured in the range $2 < \Theta < 30°$ of which 1207 were considered as observed with the criterion $I > 2\sigma(I)$. Two standard reflections were monitored every 100 min. No decomposition was detected during processing; corrections were made for Lorentz and polarization effects. Structure was solved by direct and Fourier methods and refined by full-matrix least-squares procedures, minimizing $\Sigma w(\Delta F)^2$, with isotropic temperature factors. An absorption correction following the DIFABS procedure[7] was applied to isotropically refined data, the maximum and minimum absorption factors being 0.994 and 0.681 respectively. Refinement was continued by full-matrix least-squares with anisotropic temperature factors. Hydrogen atoms were located from different synthesis and included with isotropic temperature factors. Final refinement led to R= 0.075 and R_w= 0.073 with w from an empirical weighting scheme that fits so as to give no trends in $<w\Delta^2F>$ vs. F_o and sin Θ/λ;[8] $(\Delta/\sigma)_{max}$= 0.05 and residual electronic density in final difference map 0.20 eÅ^{-3}, S= 0.866.

The atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974).[9] The computation was performed on a Vax 11/750 with MULTAN 80,[10] XRAY 76,[11] and PARST[12] programs.

^1H Nmr spectra were obtained at 293 K on a Varian XL-300 spectrometer operating at 300 MHz, using $CDCl_3$ and DMSO-d_6 as solvents and TMS as internal standard. Typical acquisition parameters were: spectral width, 5 KHz; data size, 32 K; acquisition time, 3 s; and pulse width, 8 μs (53°). In order to assign and determine chemical shifts and coupling constants, computer assisted analysis and 2D scalar shift correlated ^1H nmr experiments were performed. The computer assisted analysis of four and eight spin systems were performed with the iterative program PANIC 81 on a Bruker Aspect 2000 computer. The eight spin systems were treated like two subsystems of four spins, using an additional routine for obtaining the experimental envelope. The error of the chemical shifts and coupling constants were estimated to be ± 0.03 Hz and ± 0.05 Hz respectively and the RMS value was 0.06. 2D experiments were carried out with the same spectrometer using the COSY-90 pulse sequence. The following parameters were used: number of increments, 128; pulse width, 13.5 μ s; relaxation delay, 1 s; sweep width, ±200 Hz in t_1 and 400 in t_2 and 256x256 transformed data points.

Ir spectra were recorded on a Perkin-Elmer 599B spectrophotometer. Indene and polystyrene were used for instrument calibration. All compounds were compressed into KBr pellets. Spectra in chloroform (~0.05 M; l= 0.02 cm), and deuterated dimethyl sulfoxide solutions were also recorded. Spectra for very dilute carbon tetrachloride solutions (0.001 M) in the 3600-2400 cm^{-1} region were also taken using 4 cm quartz cells.

Raman spectra were measured for some samples on a Jobin Yvon U 1000 spectrometer using argon radiation at 514.5 nm and krypton radiation at 647.1 nm. The samples were in the form of powder.

Uv spectra were recorded on a Bausch and Lomb Spectronic 2000 spectrophotometer. The solutions were in the range of concentration of 10^{-5} M.

Melting points are uncorrected and were measured on a Büchi capillary melting point apparatus. All compounds gave elemental analysis according to their structures.

The synthesis of compounds 1, 2, 3, and 4a is already reported.[13] The $4b_4$ form of tris(2-benzothiazolyl)methane was obtained together with 4a when 4a was crystallized in benzene in the presence of catalytic amounts of acetic acid. The other samples were obtained as follows:

Tris(2-benzothiazolyl)methane, $4b_1$.

A solution of 0.01 mol (2.8 g) of bis(2-benzothiazolyl)methane[14] in 20 ml of dry DMF was added over a suspension of 0.01 mol (0.3 g of NaH 80%) of sodium hydride in 10 ml of dry DMF under N_2 atmosphere and external cooling with an ice-water bath, after which, a solution of 0.005 mol (1.06 g) of 2-methylsulfonylbenzothiazole[15] in 5 ml of dry DMF was also added. The stirring was continued for further 4 h at room temperature and the final reaction mixture was filtered. The addition of water to the filtered solution afforded a precipitate which was filtered and crystallized from benzene. The yield was 50%, mp 267-269 °C. Anal. Calcd for $C_{22}H_{13}N_3S_3$: C, 63.59; H, 3.15; N, 10.11 %. Found: C, 63.61; H, 3.50; N, 10.52 %.

1,1-Bis(2-benzothiazolyl)-1-phenylethane, 5.

Butyllithium (3.75 ml of 1.6 M solution) was added over a solution of 0.005 mol (1.79 g) of 1 in 60 ml of THF at -10 °C under N_2 atmosphere, followed by addition of 0.006 mol (0.852 g) of methyl iodide in THF (10 ml). The reaction mixture was kept at room temperature for 4 h and then refluxed 18 h. The mixture was poured onto ice-water, extracted with ether, and the ethereal layers were dried over anhydrous sodium sulfate and concentrated under "vacuum". The crude product obtained was purified by columm chromatography over aluminium oxide with hexane-chloroform (10:3) as eluent. Compound 5 was obtained in 31 % yield, mp 114-117 °C (ethanol). Anal. Calcd for $C_{22}H_{16}N_2S_2$: C, 70.93; H, 4.33; N, 7.52 %. Found: C, 71.17; H, 4.68; N, 7.81 %.

Phenyl-2-benzothiazolyl-3-methyl-2,3-dihydro-2-benzothiazolilidenemethane, 6.

A mixture of 0.01 mol (3.58 g) of 1 and 0.01 mol (1.51 ml) of methyl p-toluenesulfonate was heated at 180 °C for 3 h. The solid residue was treated with chloroform and water, and the organic layer was dried over anhydrous magnesium sulfate and concentrated under "vacuum". The treatment of the residue with ethanol and ether gave a solid which was filtered and identified as 6, with a yield of 19 %, mp 207-209 °C (ethanol). Anal. Calcd for $C_{22}H_{16}N_2S_2$: C, 70.93; H, 4.33; N, 7.52 %. Found: C, 70.82; H, 4.13; N, 7.47 %.

2-Benzothiazolyl-diphenylmethane, 7.

To a solution of 0.03 mol (3.75 g) of o-aminothiophenol and 43 g of polyphosphate ester[16] in 50 ml of chloroform (dried over phosphorous pentoxide), 0.045 mol (9.54 g) of diphenylacetic acid was added, and the whole was refluxed for 30 min. The mixture reaction was concentrated and neutralized with a cold aqueous solution of sodium bicarbonate. The crude solid thus obtained was filtered and extracted with petroleum ether to give 7 after evaporation. Yield, 64 %, mp 88-90 °C (ethanol), (lit.[17] mp 89-91 °C from methanol). Anal. Calcd for $C_{20}H_{15}NS$: C, 79.70; H, 5.02; N, 4.65 %. Found: C,79.57; H, 5.00; N, 4.62 %.

ACKNOWLEDGEMENTS

One of the authors (M.T.R.) gratefully acknowledges an investigation grant of the Plan Nacional de Formación de Personal Investigador.

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Received, 8th August, 1988