^{13}C NMR and Crystallographic Study of Thymolsulfonephthalein

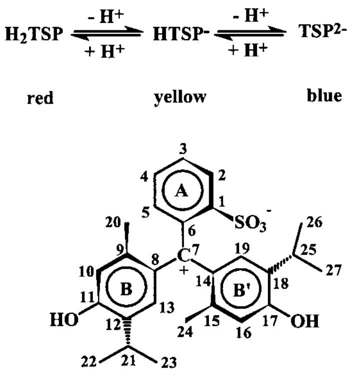
Rosa Santillan,* Norberto Farfán, Dolores Castillo, Atilano Gutiérrez, and Herbert Höpfl

Abstract: Up to now the correct structure of the undissociated thymolsulfonephthalein has not been determined unequivocally and three possible resonance structures have been proposed so far: a zwitterionic one, a quinoid one, and a lactonoid one. The present ^{13}C NMR and X-ray crystallographic study resolves this problem and it can be explicitly shown that the correct structure is zwitterionic with some delocalization of positive charge into the phenol rings. The correct assignment of the completely dissociated blue basic form is also included and permits the conclusion that a fourfold-charged resonance structure is as probable as a quinoid one.

Keywords: NMR spectroscopy · solid-state structures · structure elucidation · thymolsulfonephthalein · zwitterionic states

Introduction

Thymolsulfonephthalein **1**, also known as thymol blue, is a widely used acid/base indicator that dissociates in two steps (Scheme 1).[1–3] The pK$_a$ values for deprotonation are solvent dependent: pK$_{a1}$ (H$_2$O) = 1.7, pK$_{a1}$ (MeOH) = 4.9, pK$_{a2}$ (H$_2$O) = 9.2, and pK$_{a2}$ (MeOH) = 12.7.[3] Although sulfonephthaleins have been widely studied in this century, there is still some doubt about their molecular structures. The extremely insoluble undissociated acid form especially is still a subject of discussion,[1, 2, 4–6] and three possible structures have been proposed: a zwitterionic one (**1a**), a quinoid one (**1b**) and a lactonoid one (**1c**). With respect to the monoanion and the dianion, the quinoid structures **2** and **3** have been proposed.[2, 6]



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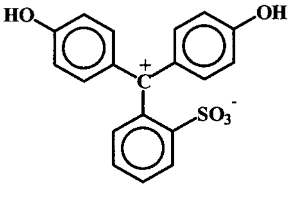
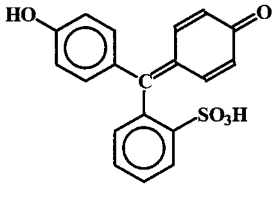
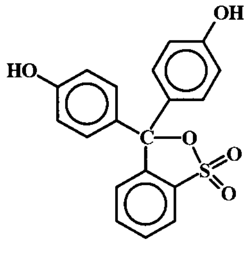
Scheme 1. The two dissocaition steps of thymolsulfonephthalein.



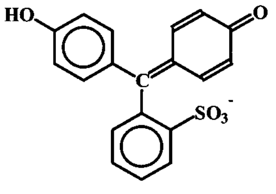
1a



1b



1c



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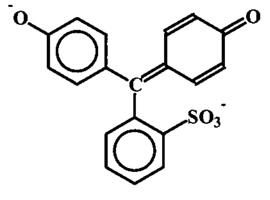

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These proposals require that at least one of the phenyl rings is located in the plane of the three central coplanar bonds. This is in contrast to X-ray crystallographic studies of triarylcarbenium ions[7] in which only structures with twisted

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Table 1. ^{13}C[a] and ^{1}H[b] NMR data (δ) of the undissociated (H_2TSP) and completely dissociated (TSP^{2-}) form of thymolsulfonephthalein in CD_3OD at pH < 2.

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8) C(14)	C(9) C(15)	C(10) C(16)	C(11) C(17)	C(12) C(18)	C(13) C(19)
H_2TSP	147.39	130.15	133.58	131.24	133.73	140.91	190.19	135.67	150.67	122.09	169.53	136.64	142.14
								135.98	150.80		170.07		143.20
TSP^{2-}	146.16	129.72	130.09	130.33	133.77	142.77	170.17	130.78	145.93	126.16	179.64	138.17	137.64
								131.34	146.09	126.54	180.43	138.72	139.31
		H(2)	H(3)	H(4)	H(5)					H(10) H(16)			H(13) H(19)
H_2TSP		8.14	7.76	7.59	7.08					6.80			6.94
										6.85			7.04
TSP^{2-}		8.08	7.52	7.44	7.02					6.33			6.77
										6.38			6.88

[a] H_2TSP: δ(20-CH_3 and 24-CH_3) = 21.89 and 21.95, δ(21-CH and 25-CH) = 27.85, δ(*i*pr-CH_3) = 22.15 and 22.29; TSP^{2-} : δ(20-CH_3 and 24-CH_3) = 22.19, δ(21-CH and 25-CH) = 26.93 , δ(*i*pr-CH_3) = 22.77, 22.98, 23.05 and 23.11. [b] H_2TSP: δ(20-CH_3 and 24-CH_3) = 1.92 and 2.00, δ(21-CH and 25-CH) = 3.13 and 3.18, δ(*i*pr-CH_3) = 1.07, 1.08, 1.12 and 1.14; TSP^{2-}: δ(20-CH_3 and 24-CH_3) = 1.78 and 1.89, δ(21-CH and 25-CH) = 3.15 and 3.19, δ(*i*pr-CH_3) = 0.97, 0.98, 1.02 and 1.04.

aromatic rings have been observed. Similar results are provided by ^{19}F NMR conformational studies of different *meta*-substituted (by fluorine) triphenylcarbenium ions.[8] In both cases propeller conformations have been found to be the most stable ones as a result of steric repulsion between the *ortho*-hydrogen atoms. A series of sulfonephthaleins (xylenol blue, cresol purple, bromoxylenol blue, bromothymol blue, bromocresol green, etc.) including thymol blue carries substituents in the *ortho* position of the phenyl rings, so that propeller conformations should be expected, especially in these cases.

In the present contribution the completely assigned ^{13}C NMR spectrum of the red acid form of thymolsulfonephthalein **1** is presented for the first time, together with a crystallographic study. It will be demonstrated that the correct structure is the zwitterionic form **1a**. The ^{13}C NMR spectrum of the corresponding basic form is also included, because former assignments still presented some faults.[2, 5]

Results and Discussion

The ^{1}H and ^{13}C NMR spectra of the undissociated and completely dissociated forms of thymolsulfonephthalein could be completely assigned by COSY, *z*-gradient HMQC, *z*-gradient HBMC, and NOESY pulse sequences and their chemical shifts are given in Table 1.

Discussion of the blue basic form (TSP^{2-}): As can be seen from Table 1, the ^{13}C NMR spectrum of the blue basic form (TSP^{2-}) consists of 19 signals in the region δ = 126–180. Six of these signals can be assigned to the asymmetric phenyl ring carrying the sulfonyl group, one signal corresponds to the central C7 carbon atom, and the other 12 signals can be assigned to the aryl rings B and B′. This observation clearly shows that a hindered rotation of the aryl rings around the C7–C8 and C7–C14 bonds occurs as a result of the methyl groups in *ortho* position. Four signals in the region of δ = 22.8–23.1 for the four *iso*-propyl methyl groups confirm this result. The central carbon atoms of the *iso*-propyl groups as well as the carbons of the *ortho*-methyl substituents are not split in the ^{13}C NMR spectrum, but their different anisotropic shielding can be seen from the ^{1}H NMR spectrum (Table 1).

The ^{13}C NMR chemical shifts of the carbon atoms C11 and C17 in the *para* position (δ = 179.6 and 180.4) present intermediate values between the displacements of the phenolate ion (δ = 168.1) and *p*-benzoquinone (δ = 187.0). The central carbon atom, which was assigned unequivocally by the *z*-gradient HBMC pulse sequence (C7 correlates with H13, H19, and H5), is shifted to high field (δ = 170.2) when compared with *para*-substituted triarylcarbenium ions ($(p\text{-}XC_6H_4)_3C^+$ with values of δ = 210.4 (X = H), 191.8 (X = OMe), and 175.5 (X = NMe_2).[9] Both observations indicate that at least a partial overlap exists between the empty p orbital of the central C7 carbon atom and the p_π orbitals of the adjacent C8 and C14 carbons, thus permitting delocalization of positive charge into the aryl rings. However, it should be noted that the central carbon atom C7 has certain carbocationic character.

Thymolsulfonephthalein can exhibit four different propeller conformations. The NOESY correlation spectrum shows interactions between the H5/Me20, Me20/H19, and Me24/H13 hydrogen atoms. Molecular modeling indicates that conformation **3a** represents the Me20–H19 interaction, con-

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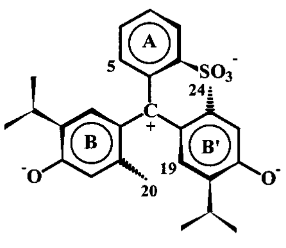
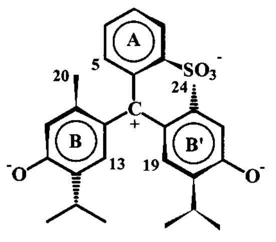
Abstract in Spanish: *Estudio de Timolsulfonftaleina por RMN de ^{13}C y Cristalografía de Rayos-X*

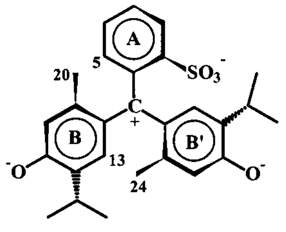
La estructura correcta de timolsulfonftaleina (Azul de timol) no ha sido establecida de manera definitiva y a la fecha se han propuesto tres estructuras de resonancia posibles: una zwitteriónica, una quinoide y una de tipo lactona. El presente estudio por RMN de ^{13}C y cristalografía de rayos-X resuelve este problema y demuestra que la estructura correcta es zwitteriónica donde existe una deslocalización de la carga positiva en los anillos fenólicos. La caracterización por RMN de la forma azul básica completamente disociada también se incluye y muestra que, en este caso, tanto la estructura quinoide como una zwitteriónica son posibles.



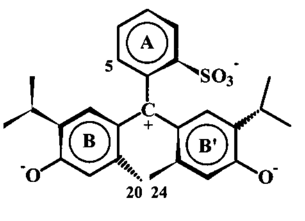
3a



3b



3c



3d

formation **3b** the H5–Me20 interaction, conformation **3c** both the H5–Me20 and H13–Me24 interactions, and conformation **3d** none of these. Therefore, it can be assumed that in solution the preferred conformation of the molecule in this study is **3c**. Nevertheless, it cannot be excluded that more than one conformation is present in solution, because dynamic interconversion processes (rotation around C7–C8 and C7–C14) must be considered on basis of the NOESY spectrum.

Discussion of the red acid form (H_2TSP): The red acid form of thymolsulfonephthalein is nearly insoluble and a good resolution in the ^{13}C NMR experiment with detection of all quaternary carbon atoms could only be achieved after about half a million transients. In this spectrum 17 signals can be observed in the region of $\delta = 122-190$. Six signals correspond to the 2-sulfonylphenyl group, one can be assigned to the central carbon atom C7, and the aryl rings B and B′ are described by the remaining 10 signals, whereby carbons C10/C16 and C12/C18 exhibit only one signal (Table 1). Different anisotropic shielding of H10/H16 can be observed from the ^1H NMR spectrum.

Figure 1 shows the long-range correlation between C7 and H5 that finally establishes the correct assignment of the central carbon atom. The comparison of the ^{13}C NMR data of the blue basic with the red acid form shows some characteristic differences for the central carbon atom and the carbons of the aryl rings B and B′, while the chemical shifts of the carbon atoms in the sulfonyl-substituted phenyl ring remain constant. In the protonated form the phenolic groups contribute less to the delocalization of the positive charge at C7, so that the chemical shifts of the *ortho*-carbons C9, C15, C13, and C19, the *ipso*-carbons C8 and C14, and the central carbon atom are significantly shifted to lower field when compared with the blue basic form. For the central carbon atom the shift difference is about $\Delta\delta = 20$ ppm, but there should still be a small $p_\pi - p_\pi$ interaction at the C7–C8 and C7–C14 bonds: the C7 displacement ($\delta = 190.2$) is high-field shifted when compared with that of the triphenylcarbenium ion ($\delta = 210.4$).[9] This argument is supported by the chemical shifts of C11 and C17 ($\delta = 169.5$ and 170.1, respectively) with values between the displacements of phenol ($\delta = 155.4$) and *p*-benzoquinone ($\delta = 187.0$). Based on these data the lactonoid form **1c** can be excluded as possible structure for the red acid form.

The NOESY experiment of the acid form evidences the interactions observed already for the blue basic form. Rotation around the C7–C8 and C7–C14 bonds was established as a result of chemical exchange between H10 and H16, Me20 and Me24, H13 and H19, and finally between H21 and H25 (Figure 2). Coalescence between each pair of the above mentioned signals is achieved at 318 K.

In order to get some more information about the three-dimensional structure of these molecules, the solid-state ^{13}C CP-MAS spectrum was recorded and three signals at $\delta = 187.8$, 190.2, and 191.8 were detected (Figure 3). This indicates

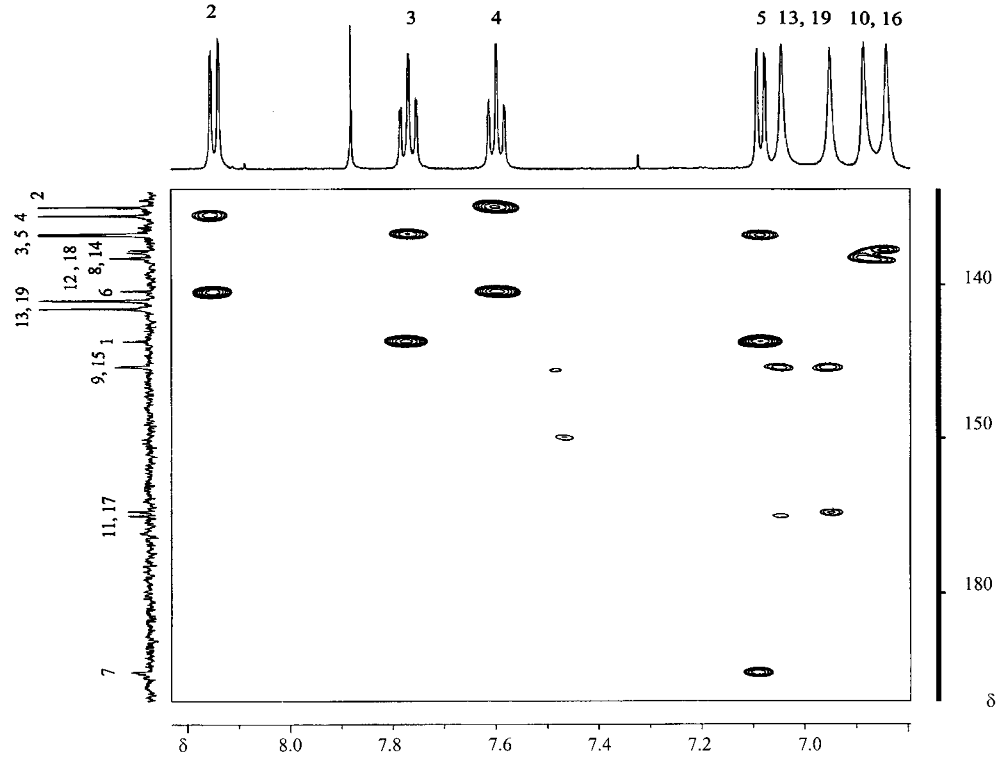


Figure 1. *z*-Gradient HMBC spectrum of undissociated thymolsulfonephthalein **1** showing the long range correlation between C7 and H5.

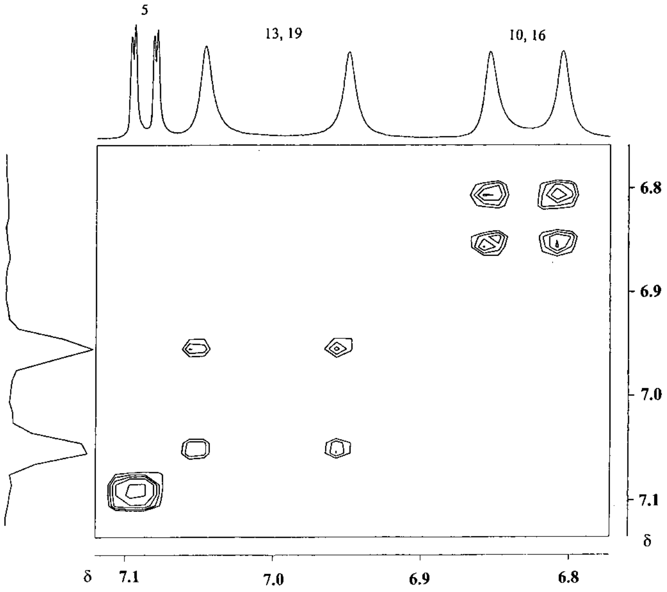


Figure 2. NOESY spectrum of undissociated thymolsulfonephthalein **1** that demonstrates the chemical exchange between H10 and H16 as well as H13 and H19.

that one of the four conformations **3a**–**3d** is highly disfavored, and we propose that it is conformation **3d**, owing to a repulsive interaction between the *ortho*-methyl groups of the two aryl rings B and B′ that is lacking in conformations **3a**–**3c**.

Crystallographic study of the red acid form (H_2TSP): The crystallographic study of the red acid form was carried out with the aim to evaluate the contributions of the zwitterionic and quinoid forms to the resonance structure of thymol blue in its undissociated form. The molecular structure of **1** is shown in Figure 4. Selected bond lengths, bond angles, torsion angles, and mean planes are summarized in Tables 2–3.

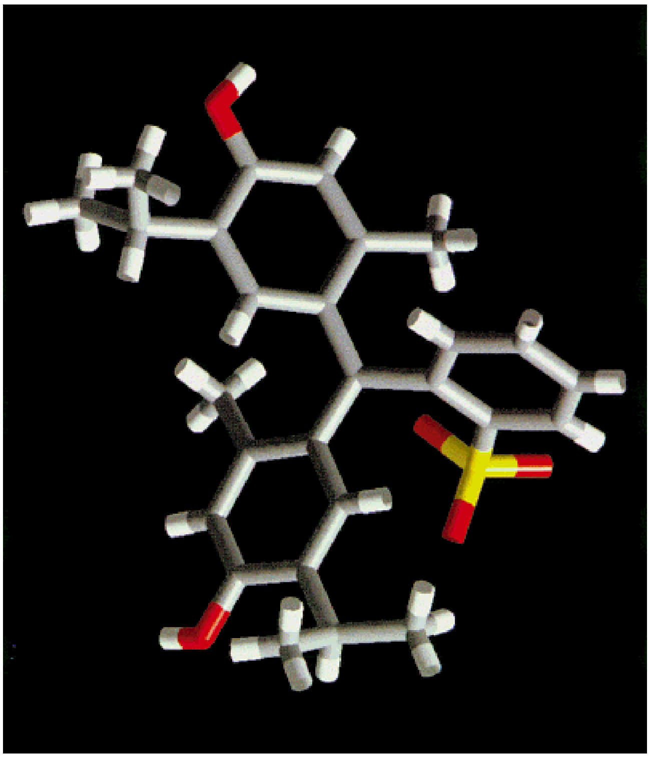


Figure 4. Molecular structure of undissociated thymolsulfonephthalein **1**.

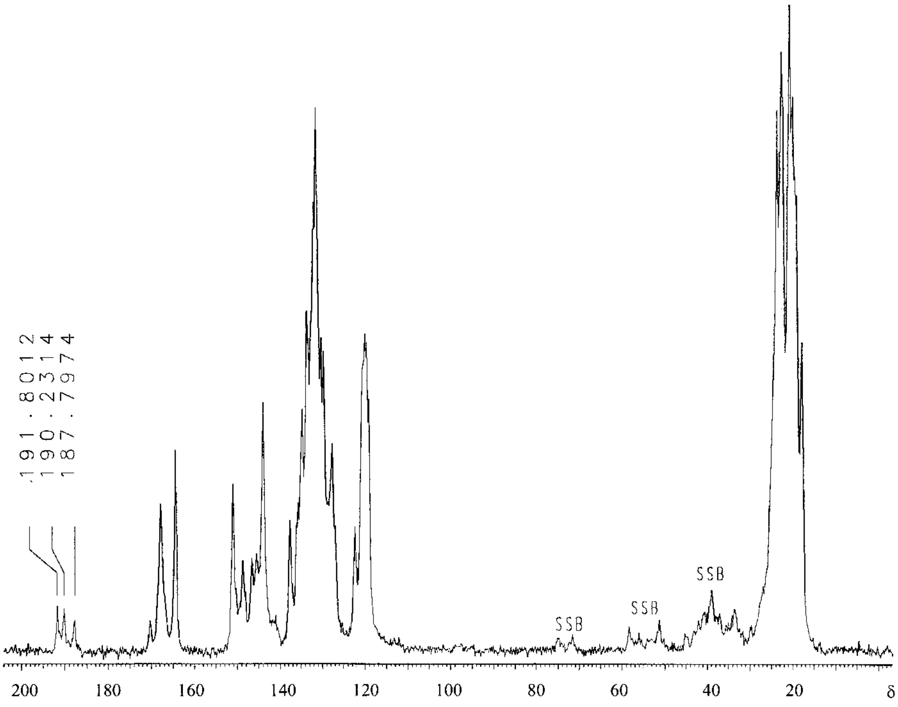


Figure 3. ^{13}C CP-MAS spectrum (at 7 kHz, CP contact time: 1.0 ms) of undissociated thymolsulfonephthalein **1**.

Since the first crystallographic study of the triphenylcarbenium ion in 1965,[10] it is known that the three aromatic rings of the cation are mutually twisted (at an angle of 45–61°)[7] in order to relieve the steric interactions between the *ortho*-hydrogen atoms of adjacent rings. Thus, the triphenylcarbenium ion exhibits a propeller shape, whereby the phenyl rings form the blades. Despite this conformation delocalization of electrons from the aromatic ring into the electron deficient central carbon atom still exists, as can be seen from the C^+–C and C–C bond lengths. An appreciable π-electron delocalization throughout the cation has also been reported for the tri(*p*-aminophenyl)carbenium ion with strong donors in *para*-position.[11]

In the case of the present thymolsulfonephthalein **1**, the molecular conformation is propeller shaped

Table 2. Selected bond lengths, bond angles, and torsion angles of thymolsulfonephthalein **1**.

Bond lengths [pm]			
S(1)–O(1)	145.0(2)	S(1)–O(2)	145.0(2)
S(1)–(3)	144.3(2)	S(1)–C(1)	179.1(2)
O(4)–C(11)	134.0(2)	O(5)–C(17)	133.7(2)
C(6)–C(7)	148.3(3)	C(7)–C(8)	142.7(2)
C(7)–C(14)	143.2(2)	C(8)–C(9)	143.2(3)
C(9)–C(10)	137.7(3)	C(10)–C(11)	139.2(3)
C(11)–C(12)	141.1(3)	C(12)–C(13)	136.9(3)
C(8)–C(13)	142.4(3)	C(14)–C(15)	143.0(3)
C(15)–C(16)	138.1(3)	C(16)–C(17)	139.6(3)
C(17)–C(18)	141.1(3)	C(18)–C(19)	137.0(3)
C(14)–C(19)	141.8(3)		
Bond angles [°]			
S(1)-C(1)-C(2)	116.6(2)	S(1)-C(1)-C(6)	123.5(1)
O(4)-C(11)-C(10)	121.3(2)	O(4)-C(11)-C(12)	117.2(2)
O(5)-C(17)-C(16)	121.1(2)	O(5)-C(17)-C(18)	117.8(2)
C(1)-C(6)-C(5)	117.9(2)	C(1)-C(6)-C(7)	126.6(2)
C(5)-C(6)-C(7)	115.5(2)	C(6)-C(7)-C(8)	119.2(2)
C(6)-C(7)-C(14)	117.3(2)	C(7)-C(8)-C(9)	124.4(2)
C(7)-C(8)-C(13)	117.6(2)	C(7)-C(14)-C(15)	123.8(2)
C(7)-C(14)-C(19)	117.7(2)	C(8)-C(7)-C(14)	122.7(2)
C(8)-C(9)-C(10)	117.7(2)	C(9)-C(10)-C(11)	122.4(2)
C(10)-C(11)-C(12)	121.4(2)	C(11)-C(12)-C(13)	116.2(2)
C(13)-C(8)-C(9)	118.0(2)	C(14)-C(15)-C(16)	117.1(2)
C(15)-C(16)-C(17)	122.9(2)	C(16)-C(17)-C(18)	121.1(2)
C(17)-C(18)-C(19)	116.1(2)	C(18)-C(19)-C(14)	124.4(2)
Torsion angles [°][a]			
C(6)-C(7)-C(8)-C(9)	– 157.9	C(6)-C(7)-C(14)-C(15)	39.1
C(1)-C(6)-C(7)-C(8)	60.3	C(1)-C(6)-C(7)-C(14)	– 129.6
C(8)-C(7)-C(14)-C(15)	– 151.2		

[a] A positive rotation is counter-clockwise from atom 1, when viewed from atom 3 to atom 2.

Table 3. Deviations from the aryl ring mean planes for thymolsulfonephthalein **1**.

Mean plane and deviations Δ [pm][a]		Mean plane and deviations Δ [pm][b]		Mean plane and deviations Δ [pm][c]	
C(1)	0.0	C(8)	– 2.8	C(14)	0.8
C(2)	– 0.5	C(9)	1.0	C(15)	– 1.6
C(3)	0.4	C(10)	1.4	C(16)	1.0
C(4)	0.1	C(11)	– 1.9	C(17)	0.5
C(5)	– 0.6	C(12)	– 0.1	C(18)	– 1.2
C(6)	0.5	C(13)	2.5	C(19)	0.5
C(7)	5.3	C(7)	– 10.4	C(7)	– 2.9

[a] Equation of the plane: $+2.24839x + 0.42326y + 10.98178z = +10.751$; [b] Equation of the plane: $-8.06987x + 7.44985y - 1.20399z = +0.470$; [c] Equation of the plane: $+1.52319x + 11.39691y + 2.88011z = +11.847$; x, y, z are orthogonal coordinates with respect to the axes a, b, c; Δ is the deviation from the mean plane.

with a mutual twist of 54.7°, 75.7°, and 76.8° between the aryl rings. The positive charge is delocalized into the phenol rings, while the negative charge is located at the sulfonyl group. An interaction between O1 or O2 and C7 can be excluded by their bond distances (O1 ⋯ C7 374 pm and O2 ⋯ C7 293 pm). All hydrogen atoms of the molecule were determined by difference Fourier maps and both hydrogen atoms of the phenolic C–OH groups were located. Thus, the solid-state structure of undissociated thymol blue **1** has mainly zwitterionic character. However, there is also some contribution of the quinoid form **1b**: the C7–C8 and C7–C14 bond lengths (142.7(2) and 143.2(2) pm, respectively) are significantly shorter than the C6–C7 bond length (148.3(3) pm), suggesting that there is delocalization from the donor atoms to the electron-deficient C$^+$ center. The average C$^+$–C bond length for a series of triphenylcarbenium ions is 143.9 pm.[7] Delocalization through the sulfonylphenyl group is lacking, if one takes the fact into consideration that C(sp^2)–C(sp^2) bonds have lengths of 146.6(5) and 147.6(6) pm.[7] The C–C bond lengths in the *para*-substituted aryl rings have average values of 142.6(3), 137.4(3), and 140.3(3) pm and vary significantly when compared with the normal value of 139.7(5) pm in benzene. The trend in these lengths also demonstrates the contribution of the quinoid canonical form in the molecular structure. Similar data have been obtained for the tri(*p*-aminophenyl)carbenium ion (142.2(10), 137.7(11), and 141.8(4) pm). The phenolic carbon–oxygen bond lengths are 134.0(2) and 133.7(2) pm and are therefore intermediate between the C=O bond length in *p*-benzoquinone (122.2 pm)[12] and the C–O bond length in phenol (136.2 pm).[13] The molecular conformation found in this crystallographic study corresponds to conformer **3c**.

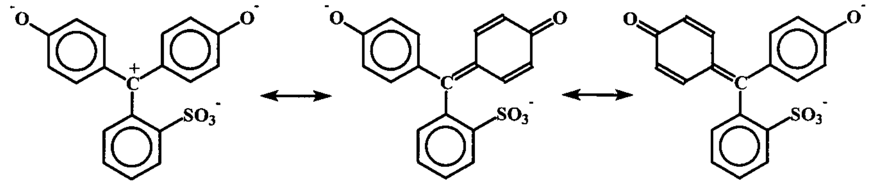
Conclusions

From the present NMR and crystallographic studies it can be concluded that the red acid form of thymolsulfonephthalein has a zwitterionic structure with some delocalization of positive charge into the phenol rings. With respect to the blue basic form, the three resonance structures can be proposed in consideration of a propeller shaped conformation (Scheme 2). Unfortunately, we did not obtain monocrystals of the monoanion and dianion salts, so that we can not be sure which form dominates in the solid state.

Experimental Section

The commercially available thymol blue (Aldrich) was recrystallized from acetic acid, and bright green crystals suitable for X-ray crystallography were obtained.

NMR measurements: ^{1}H and natural abundance ^{13}C NMR spectra were recorded on a Bruker DMX500 spectrometer at 500.13 and 125.77 MHz, respectively. A solution of the red acid form of thymolsulfonephthalein was prepared in CD$_3$OD and titrated with small amounts of HCl in H$_2$O (pH < 2). The solution of the blue basic form was prepared in CD$_3$OD by titration with NaOH in H$_2$O (pH > 12). The hydrogen and carbon chemical shifts were measured at 25 °C, with TMS as the standard. Due to the low solubility of the undissociated species, the ^{13}C NMR spectrum of **1** was recorded with more than 484 000 transients in order to observe the signals of all carbon atoms, while in the case of the dianion only about 4000 transients were necessary. COSY, z-gradient HMQC, z-gradient HBMC,



Scheme 2. Resonance structures proposed for the blue basic form.

and NOESY pulse sequences were used to allow assignment of all the signals. The ^{13}C CP-MAS spectrum of **1** was recorded on a Bruker ASX300 spectrometer, with a 4 mm CP-MAS probe at 75.47 MHz and spinning at 7 kHz.

X-ray crystallography: Crystal data for $C_{27}H_{34}O_5S \cdot 4/3\,H_2O$: $M = 470.62\ \mathrm{g\,mol^{-1}}$, crystal dimensions $0.31 \times 0.36 \times 0.50\ \mathrm{mm^3}$, bright green cubes, triclinic, space group $P\bar{1}$ (no. 2), $a = 1113.31(5)$, $b = 1191.11(9)$, $c = 1243.15(7)$ pm, $\alpha = 62.967(5)^\circ$, $\beta = 66.302(4)^\circ$, $\gamma = 85.918(5)^\circ$, $V = 1.3320(2) \times 10^9\ \mathrm{pm^3}$ by least squares refinement on diffractometer angles for 24 automatically centered reflections, $Z = 2$, $D_x = 1.22\ \mathrm{g\,cm^{-3}}$, $\mu = 1.5\ \mathrm{cm^{-1}}$, no absorption correction was applied ($C_{min/max} = 0.928/0.955$), corrections were made for Lorentz and polarization effects. Data collection: Enraf Nonius CAD4 diffractometer, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71069$ Å, monochromator: graphite, $T = 293$ K, ω-2θ scan, range $2^\circ < \theta < 29^\circ$ ($\pm h$, $\pm k$, $-l$), 7355 reflections measured, of which 7037 were independent and 4874 observed $[F > 3\sigma(F)]$. Two standard reflections were monitored periodically; they showed no significant change during data collection. Structure analysis and refinement: direct methods (SHELXS-86) for structure solution. Computations were performed by means of the program CRYSTALS.[14] Atomic form factors for neutral C, O, S, and H were taken from reference [15]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were determined by difference Fourier maps; their positions (not for the crystal water) and one overall isotropic parameter were refined. One of the water molecules has an occupation factor of 1/3 and the other one is disordered with respect to the hydrogen atoms. Full-matrix least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ having values of $R = 0.044$, $R_w = 0.041$ from 4874 reflections with $I > 3\sigma(I)$ for 419 variables against $|F|$, $w = 1/\sigma^2(F)$, $s = 2.98$. Largest peaks in the rest density map: $\Delta\rho_{max} = 0.26$, $\Delta\rho_{min} = -0.37\ \mathrm{e\,Å^3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101011. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

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