1001. *Methanesulphonyl and Benzenesulphonyl Derivatives of Benzimidazolin-2-one.*

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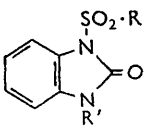
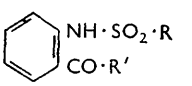
Methanesulphonyl and benzenesulphonyl derivatives of benzimidazolin-2-one have been prepared; their infrared spectra are discussed in relation to those of the corresponding acetyl and benzoyl derivatives. The interpretation of the 1700—1800 cm.$^{-1}$ region in these compounds is difficult since the number of strong bands is often greater than the number of C=O groups.

Harrison and Smith [1] recorded infrared spectra of a number of 1-acyl- and 1,3-diacylbenzimidazolin-2-ones. Two or three strong bands were observed in the 1700—1800 cm.$^{-1}$ region, but assignment to individual C=O groups was not attempted. Kew and Nelson [2] later determined spectra of some 1-acylbenzimidazolin-2-ones and claimed that such assignments could be satisfactorily made. The ring-carbonyl group was associated with a band in the region 1730—1740 cm.$^{-1}$, and the carbonyl group of the substituent with the second band. This was supported by the behaviour of the latter band on passing from the 1-acetyl to the 1-benzoyl compound. However, we still believe that these bands should not be rigidly assigned to individual carbonyl groups. The present work on substituted benzimidazolin-2-ones in which the substituents are sulphonyl instead of acyl groups strongly supports this view. Since the completion of this work, Cheetham, Forbes, Kew, and Nelson [3] have recorded, briefly, some infrared data for diacylbenzimidazolin-2-ones. Again, these authors associated a band (in this case near 1768 cm.$^{-1}$) with the ring-carbonyl group and other bands at lower frequencies with the acyl groups.

1-Methanesulphonylbenzimidazolin-2-one (I; R = Me, R′ = H) was conveniently prepared from 1-isopropenylbenzimidazolin-2-one by conversion of the latter into its 3-methanesulphonyl derivative from which the isopropenyl group was removed by acid hydrolysis. Treatment of *o*-aminobenzoyl azide in pyridine with methanesulphonyl



(I)



(II)

chloride gave *o*-methanesulphonamidobenzoyl azide (II; R = Me, R′ = N_3), decomposition of which in boiling xylene also afforded 1-methanesulphonylbenzimidazolin-2-one.

[1] Harrison and Smith, *J.*, 1961, 4827.
[2] Kew and Nelson, *Austral. J. Chem.*, 1962, **15**, 792.
[3] Cheetham, Forbes, Kew, and Nelson, *Austral. J. Chem.* 1963, **16**, 729.

1-Benzenesulphonylbenzimidazolin-2-one was prepared and its structure established by similar methods. Unexpectedly, the azides (II; R = Me and Ph, R′ = N_3) could not be obtained by the action of nitrous acid on the corresponding hydrazides (II; R′ = NH·NH_2); the poor solubility of the hydrazides in dilute hydrochloric acid may be partly responsible.

The disubstituted benzimidazolin-2-ones (I; R = Me and Ph, R′ = SO_2·Me and SO_2·Ph) were prepared by the action of the appropriate sulphonyl chloride on the disodium salt of benzimidazolin-2-one, a method previously used by Heller *et al.*[4] for the dibenzoyl compound. 1-Acetyl-3-methanesulphonylbenzimidazolin-2-one was prepared by treatment of the 1-methanesulphonyl compound with acetyl chloride or of the 1-acetyl compound with methanesulphonyl chloride.

Details of the infrared spectra (1700—1800 cm.$^{-1}$ region only) of the methanesulphonyl and benzenesulphonyl derivatives of benzimidazolin-2-one are given in Table 1: all values quoted are for sharp, very strong peaks. Only the monosubstituted compounds were sufficiently soluble in non-polar solvents for spectroscopic study.

For benzimidazolin-2-one,* even at high resolution, a single sharp band was observed

TABLE 1.

Infrared absorption bands for substituted benzimidazolin-2-ones.

		$\nu_{max.}$ (cm.$^{-1}$)		
1-Subst.	3-Subst.	KBr disc	Nujol mull	CCl_4
Me·SO_2	H	1722	1720	1729
		1746	1742	1755
Ph·SO_2	H	1717	1714	1712
		1759	1756	1755
Me·SO_2	Me·SO_2	1749	1751	
Ph·SO_2	Ph·SO_2	1762	1760	

at 1741 cm.$^{-1}$ (KBr disc). Similar single bands, but at higher frequencies, were present in the spectra of the dimethanesulphonyl- and dibenzenesulphonyl-benzimidazolin-2-ones, thus confirming the structures assigned to these compounds. The shift to higher frequencies is probably due to the electron-attracting effect (largely inductive) of the substituents, although the removal of any possibility of hydrogen bonding may also be relevant. A similar but smaller displacement of the carbonyl band would be expected for the monomethanesulphonyl- and monobenzenesulphonyl-benzimidazolin-2-ones, and this was observed. However, a second very strong band was present near 1720 cm.$^{-1}$ in both cases. It is not unusual to find two strong bands in this region when only one C=O group is present. A closely related example is 3-phenyl-1-toluene-*p*-sulphonyloxindole [7] (1724 and 1689 cm.$^{-1}$).

TABLE 2.

Infrared absorption bands for substituted benzimidazolin-2-ones.

		$\nu_{max.}$ (cm.$^{-1}$)	
1-Subst.	3-Subst.	KBr disc	Nujol mull
Ac	H	1710vs, 1733vs, 1745vs	1707vs, 1729vs, 1741vs
Bz	H	1691vs, 1731vs	1694vs, 1731vs
Ac	Ac	1721vs, 1752s, 1767vs	1721vs, 1751s, 1768vs

In view of these observations, we have redetermined the spectra of some mono- and di-acylbenzimidazolin-2-ones. Strong bands in the 1600—1800 cm.$^{-1}$ region are given in Table 2. It can be seen that the number of peaks in the carbonyl stretching region may

* The discrepancy noted by Kew and Nelson [2] between the values recorded in the literature [5,6] is partly due to an error in the value (1750 cm.$^{-1}$) previously published from these laboratories.

[4] Heller, Buchwaldt, Fuchs, Kleinicke, and Kloss, *J. prakt. Chem.*, 1925, **111**, 1.
[5] Harrison and Smith, *J.*, 1959, 3157.
[6] Mason, *J.*, 1957, 4874.
[7] Bruce and Sutcliffe, *J.*, 1957, 4789.

exceed the number of structurally different carbonyl groups. It is not improbable that these bands arise from strongly coupled vibrations as suggested for example in the case of diacylanilines.[8] Nevertheless the available results support the view [2] that the positions of the lower-frequency bands in the spectra of acylbenzimidazolin-2-ones are determined largely by the identity of the acyl groups.

Kew and Nelson [2] quoted a value of 1715 cm.$^{-1}$ for the carbonyl band in the spectrum of 1-acetylbenzimidazoline-2-thione, either as a paraffin mull or in tetrahydrofuran, and used this to support their assignment of the lower-frequency band of 1-acetylbenzimidazolin-2-one to the acetyl group. In the later Paper,[3] a value of *ca.* 1730 cm.$^{-1}$ was given for the same band, and it was implied that this had significance in relation to the spectra of 1,3-diacylbenzimidazolin-2-ones. Although the use of a different solvent (carbon tetrachloride) for the spectra recorded in the second Paper may account for a small shift, we have little confidence in arguments based on these values. We have determined the spectrum of 1-acetylbenzimidazoline-2-thione and find a strong band at 1728 cm.$^{-1}$ (KBr disc).

Apart from the 1700—1800 cm.$^{-1}$ region, the infrared spectra of the methanesulphonyl and benzenesulphonyl derivatives of benzimidazolin-2-one are quite normal. The SO_2 group stretching frequencies appear as strong bands in the regions 1360—1380 and 1170—1180 cm.$^{-1}$. The disubstituted compounds absorb only weakly above 3000 cm.$^{-1}$ (absence of N–H), but the monosubstituted compounds show one or two strong bands in this region.

Experimental

Infrared spectra were determined with a Unicam S.P. 100 instrument.

1-*Benzenesulphonylbenzimidazolin-2-one.*—(*a*) To sodium (0·42 g.) in ethanol (9 ml.) was added a solution of 1-isopropenylbenzimidazolin-2-one [9] (3 g.) in ethanol (15 ml.), followed by benzenesulphonyl chloride (2·2 ml.). The mixture was boiled under reflux for 2 hr., the ethanol removed by distillation, and the residue boiled with N-sulphuric acid (30 ml.). Addition of sufficient ethanol to give a clear solution at the b. p., and subsequent cooling, afforded 1-*benzenesulphonylbenzimidazolin-2-one* (2·1 g.) which, after recrystallisation from ethanol, formed plates, m. p. 234—235° (Found: C, 56·6; H, 3·5; N, 10·5; S, 12·0. $C_{13}H_{10}N_2O_3S$ requires C, 56·9; H, 3·7; N, 10·2; S, 11·7%).

(*b*) Benzenesulphonyl chloride (0·5 ml.) was added to a stirred solution of *o*-aminobenzoyl azide [10] (0·3 g.) in pyridine (0·75 ml.). After 30 min., water (5 ml.) was added. The yellow precipitate was collected, washed with water, and dried *in vacuo*, giving o-*benzenesulphonamidobenzoyl azide* (0·25 g.) which, on cautious recrystallisation from ethanol, formed yellow needles, m. p. 104—105° (Found: C, 52·0; H, 3·4; N, 18·6; S, 10·6. $C_{13}H_{10}N_4O_3S$ requires C, 51·7; H, 3·3; N, 18·5; S, 10·6%). The crude azide (0·3 g.) in xylene (5 ml.) was boiled under reflux for 15 min. The solid (0·15 g.) which separated afforded, on recrystallisation from aqueous ethanol, 1-benzenesulphonylbenzimidazolin-2-one, m. p. 234—235°, not depressed on admixture with material prepared by method (*a*).

1-*Methanesulphonylbenzimidazolin-2-one.*—(*a*) By a method similar to the above, 1-isopropenylbenzimidazolin-2-one (3 g.) and methanesulphonyl chloride (1·4 ml.) gave 1-*methanesulphonylbenzimidazolin-2-one* (2·0 g.) which formed needles, m. p. 183—184°, from aqueous ethanol (charcoal) (Found: C, 45·5; H, 4·1; N, 13·1; S, 15·2. $C_8H_8N_2O_3S$ requires C, 45·3; H, 3·8; N, 13·2; S, 15·1%).

(*b*) Treatment of *o*-aminobenzoyl azide (0·65 g.) in pyridine (1·5 ml.) with methanesulphonyl chloride (0·7 ml.) afforded a crude azide (0·5 g.) which was decomposed by the method used for the benzenesulphonyl compound to give 1-methanesulphonylbenzimidazolin-2-one (0·13 g.), m. p. and mixed m. p. 183—184°.

1,3-*Dibenzenesulphonylbenzimidazolin-2-one.*—A mixture of the disodium salt of benzimidazolin-2-one [4] (1 g.), benzene (8 ml.) and benzenesulphonyl chloride (1·9 ml.) was kept at

[8] Abramovitch, *J.*, 1957, 1413.
[9] Davoll, *J.*, 1960, 308.
[10] Heller and Siller, *J. prakt. Chem.*, 1926, **116**, 9.

room temperature for 2 days with occasional shaking. The solid was collected and extracted three times with boiling benzene. On cooling, the extracts afforded 1,3-*dibenzenesulphonylbenzimidazolin-2-one* (0·7 g.) as needles (from benzene), m. p. 201—203° (Found: C, 55·4; H, 3·6; N, 6·8; S, 15·2. $C_{19}H_{14}N_2O_5S_2$ requires C, 55·1; H, 3·4; N, 6·8; S, 15·5%).

1,3-*Dimethanesulphonylbenzimidazolin-2-one*.—By a method similar to that used for the dibenzenesulphonyl derivative, 1,3-*dimethanesulphonylbenzimidazolin-2-one* was obtained as needles (from benzene), m. p. 247—248° (Found: C, 37·3; H, 3·4; N, 9·5; S, 22·2. $C_9H_{10}N_2O_5S_2$ requires C, 37·2; H, 3·4; N, 9·7; S, 22·1%).

1-*Acetyl*-3-*methanesulphonylbenzimidazolin-2-one*.—To 1-methanesulphonylbenzimidazolin-2-one (0·2 g.) in pyridine (3 ml.) at 0° acetyl chloride (0·3 ml.) was added dropwise with shaking. After 15 min., water (10 ml.) was added and the solid collected (0·15 g.). Crystallisation from benzene afforded 1-*acetyl*-3-*methanesulphonyl-benzimidazolin-2-one* as needles, m. p. 166—167° (Found: C, 47·6; H, 4·0; N, 10·7; S, 12·6. $C_{10}H_{10}N_2O_4S$ requires C, 47·2; H, 3·9; N, 11·0; S, 12·6%), $\nu_{max.}$ 1765vs, 1721vs (KBr disc). An identical product was obtained from 1-acetylbenzimidazolin-2-one and methanesulphonyl chloride in pyridine.

Methyl o-*Methanesulphonamidobenzoate*.—Methanesulphonyl chloride (8 g.) was added with cooling and shaking to methyl anthranilate (10 g.) in pyridine (20 ml.). After addition of water, the solid was collected and washed with water, giving the *methanesulphonyl derivative* (12·0 g.). Recrystallisation from ethanol (charcoal) gave plates, m. p. 89—90° (Found: C, 47·15; H, 5·0; N, 5·9; S, 14·0. $C_9H_{11}NO_4S$ requires C, 47·2; H, 4·8; N, 6·1; S, 14·1%).

o-*Methanesulphonamidobenzhydrazide*.—A mixture of methyl *o*-methanesulphonamidobenzoate (3 g.) and 98% hydrazine hydrate (1 ml.) was heated under reflux on the steam-bath for 1 hr. On cooling, the *hydrazide* separated as a solid (2·5 g.), which was washed with ethanol and with ether, and then recrystallised from ethanol (charcoal), giving needles, m. p. 132—133° (Found: C, 41·9; H, 4·8; N, 18·2; S, 13·8. $C_8H_{11}N_3O_3S$ requires C, 41·9; H, 4·8; N, 18·3; S, 14·0%). The *isopropylidene derivative* formed needles (from acetone), m. p. 148—149° (Found: C, 49·3; H, 5·6; N, 15·4; S, 11·7. $C_{11}H_{15}N_3O_3S$ requires C, 49·1; H, 5·6; N, 15·6; S, 11·9%).

o-*Benzenesulphonamidobenzhydrazide*.—Methyl *o*-benzenesulphonamidobenzoate (3 g.) and 98% hydrazine hydrate (1 ml.) gave the *hydrazide* (2·9 g.) which afforded needles, m. p. 95—96°, from ethanol (charcoal) (Found: C, 53·6; H, 4·5; N, 14·7; S, 11·05. $C_{13}H_{13}N_3O_3S$ requires C, 53·6; H, 4·5; N, 14·4; S, 11·0%). The *isopropylidene derivative* formed needles (from acetone), m. p. 191—192° (Found: C, 58·3; H, 5·6; N, 12·7; S, 10·0. $C_{16}H_{17}N_3O_3S$ requires C, 58·0; H, 5·1; N, 12·7; S, 9·7%).

Action of Nitrous Acid on o-*Sulphonamidobenzhydrazides*.—To *o*-benzenesulphonamidobenzhydrazide (1 g.) in 6N-hydrochloric acid (100 ml.), sodium nitrite (0·25 g.) in water (25 ml.) was added dropwise with stirring, at 0—5°. The solid (1 g.) was collected and after recrystallisation from ethanol had m. p. 95—96°, not depressed on admixture with starting material. Similarly *o*-methanesulphonamidobenzhydrazide was recovered unchanged after treatment with nitrous acid.

The following compounds were prepared by recorded methods: 1-acetyl-, 1-benzoyl-, and 1,3-diacetyl-benzimidazolin-2-one [1] and 1-acetylbenzimidazolin-2-thione.[2]

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