A physical Study on the Aromaticity of 4H-Pyran-4-one, 9H-Xanthen-9-one, and related sulphur Compounds

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Dipole moment analysis of 4H-pyran-4-one and 9H-xanthen-9-one, and their sulphur analogues, and of 9H-selenoxanthen-9-one, enables a discussion on their aromaticities. In the present work, the dipole moments of tetrahydro-4H-pyran-4-one, tetrahydrothio-4H-pyran-4-one, tetrahydroseleno-4H-pyran-4-one, 9(10H)-anthracen-9-one, 9H-xanthen-9-one, 9H-thioxanthen-9-one and 9H-selenoxanthen-9-one were measured in benzene solution at 30.0 °C.

Introduction

The 4H-pyran-4-one ring occurs in a number of biological compounds such as meconic acid present in opium, kojic acid: an antibiotic substance produced in an aerobic process by a variety of microorganisms from a wide range of carbon sources, yangonin existing in Kawa roots [1]. Recently lateopyron, a new antibiotic, has been isolated from fungus Fusarium lateritium Nees and the X-ray structure of its dimethyl derivative determined [2]. Euxanthon exists in the urine of cows fed with mango-tree leaves, and gentisin occurs in gentian [1].

Some chemical properties support that 4H-pyran-4-one is weakly aromatic [3]; for instance, nitration of the compound gives 3-nitro-4H-pyran-4-one, with a very low yield however. Some of its physicochemical data also are consistent with a slight aromatic character (see [4] and [5] for relevant references). 9H-xanthen-9-one appears to be aromatic, following its diamagnetic susceptibility [6].

Since the aromaticity of 4H-pyran-4-one can be related to contribution of the valence structure (IV) which contains a benzene-like π-sextet, the (O...C=O) interaction moment may give some information in this respect (vide infra).

In the present work, the electric dipole moments of tetrahydro-4H-pyran-4-one (**1**-a), tetrahydrothio-4H-pyran-4-one (**1**-b), tetrahydroseleno-4H-pyran-4-one (**1**-c), 4H-pyran-4-one (**2**-a), 9(10H)-anthracen-9-one (anthrone) (**3**), 9H-xanthen-9-one (xanthone) (**3**-a), 9H-thioxanthen-9-one (**3**-b) and 9H-selenoxanthen-9-one (**3**-c) were determined in benzene solution at 30.0 °C.

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Experimental

Synthetic

1-a, b.p. 65 °C at 15 mmHg (lit. 60–61 °C at 13 mm Hg [7]), and **1**-b, m.p. 66 °C (lit. 65–67 °C [8]), were bought from Janssen Chimica, Beerse (Belgium), and **1**-c was synthesized as indicated in Ref. [9]: m.p. 58 °C (lit. 55.0–55.5 °C [10]).

2-a, m.p. 32.5 °C (lit. 32.5–32.6 °C [11]), came from Ega-Chimie, Strasbourg (France).

3, m.p. 161 °C (lit. 163–164 °C [12]), **3**-a, m.p. 173.5 °C (lit. 177 °C [13]), and **3**-b, m.p. 207 °C (lit. 212–214 °C [14]), were bought from Janssen Chimica, Beerse (Belgium) and **3**-c, m.p. 191–192 °C (lit. 191–192 °C [15]), was prepared as indicated in [16].

Physical Measurements

The electric dipole moments were determined by using the well-known Debye refractivity method. The total polarisation of the solute, extrapolated to infinite dilution, was calculated from the experimental ratios [17],

$$\alpha_0 = \lim_{(w \to 0)} \left[\frac{\varepsilon - \varepsilon_1}{w} \right] \quad \text{and} \quad \beta = \frac{\sum (v - v_1)}{\sum w},$$

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where w is the weight fraction of the solute and ε and v are the dielectric permittivity and specific volume of the solutions, respectively. The subscript one refers to the pure solvent as used, i. e. made up in the same way as the solutions. The α_0 value was calculated from the linear function, $\alpha = \alpha_0 + \alpha' w$, obtained by least-squares analysis of the $\varepsilon(w)$ polynomial (quadratic) function.

The distortion polarization of the solute, ${}_{E}P + {}_{A}P$, was assumed to equal the molecular refraction for the sodium D line, calculated from $\sum (n^2 - n_1^2)/\sum w$ and β defined as above.

The techniques used to determine the dielectric permittivity, specific volume and refraction index of the solutions (and solvent) are described elsewhere [18, 19].

For each solute, w_{max} (here reported to only three decimal places although it is known to five or six decimal places), α_0, β (in $cm^3 g^{-1}$), $P_{2\infty}$ and R_D (both in $cm^3 mol^{-1}$), and μ in Debye units (1 D = 3.3356×10^{-30} C m) are given in Table 1.

Table 1. Physical data from dipole moment determinations in benzene solution at 30.0 °C.

Compound	w_{max}	α_0	$-\beta$	$P_{2\infty}$	R_D	μ/D
1-a	0.024	3.14	0.242	86.7	24.9	1.75
1-a [a]	0.012	5.50	−0.274	85.1	24.9	1.73 [b]
1-b	0.019	2.15	0.305	76.5	31.0	1.50 [c]
1-c	0.025	1.95	0.537	90.0	33.8	1.67
2-a	0.024	15.20	0.343	300.4	24.8	3.70 [d]
3	0.015	6.64	0.267	295.9	62.6	3.41 [e]
3-a	0.033	5.16	0.373	237.5	60.1	2.97 [f]
3-b	0.014	4.00	0.403	208.3	67.3	2.65 [g]
3-c	0.021	3.35	0.537	212.1	70.5	2.65

[a] In carbon tetrachloride.
[b] 1.720 D in the gaseous phase [20].
[c] Lit. 1.73 and 1.52 D [21].
[d] Bibl. 3.73 D in benzene [21, 22], 3.49 D in the liquid phase [23], 3.79 D in the gaseous phase [5].
[e] Lit. 3.69, 3.46, 3.62, 3.66 and 3.52 D [21], and 3.65 D [24].
[f] Bibl. 2.94, 3.10, 2.95, 3.14, 3.01 and 2.94 D [21], 3.01 D [22], and 2.96 D [25].
[g] Lit. (5.4), 2.75, 2.75 and 2.59 D [21], 2.75 D [22], and 2.62 D [25].

Results and Discussion

Table 2 lists the dipole moments of the compounds here studied, as well as those of other derivatives calculated by additivity or measured in benzene solution.

1) Tetrahydro-4H-pyran-4-one **1**-a [20], tetrahydrothio-4H-pyran-4-one **1**-b [33] and tetrahydroseleno-4H-pyran-4-one **1**-c [10] are known to exist in a chair conformation, with some puckering of the heterocyclic ring. This is supported by their dipole moments (1.75, 1.50 and 1.67 D) being markedly greater than the values (1.47, 1.26 and 1.39 D) calculated from those of cyclohexanone (3.04 D [34]), tetrahydropyran (1.57 D [35]), tetrahydrothiopyran (1.78 D [36]), or tetrahydroselenopyran taken as $1.78 + \mu(Me_2Se) - \mu(Me_2S) = 1.78 + 1.32$ [37] − 1.45 [38] = 1.65 D. Part of the discrepancies (0.28, 0.24 and 0.28 D) may be due to induction effects through space between the heteroatom and carbonyl bond, however.

4H-pyran-4-one **2**-a, 4H-pyran-4-thione **2′**-a and 4H-thiopyran-4-thione **2′**-b are all planar molecules in the gaseous phase [5], as well as is 9H-xanthen-9-one **3**-a in the crystalline state [39]. By analogy,

Table 2. Experimental, or calculated, dipole moments of tetrahydro-4H-pyran-4-ones and -thiones (**1**-x and **1′**-x), 4H-pyran-4-ones and -thiones (**2**-x and **2′**-x), 9(10H)-anthracen-9-one and -thione (**3** and **3′**), 9H-xanthen-9-ones and -thiones (**3**-x and **3′**-x) (Debye units).

Ketone [a]	μ	Thioketone [a]	μ
1-a	1.75	**1′**-a	1.30 [c]
1-b	1.50	**1′**-b	1.05 [c]
1-c	1.67	**1′**-c	1.22 [c]
2-a	3.70 [b]	**2′**-a	4.08 [23], 4.10 [22] [b]
2-b	3.96 [28], 4.00 [22] [b]	**2′**-b	4.41 [28], 4.45 [22] [b]
3	3.41	**3′**	3.27 [d]
3-a	2.97	**3′**-a	3.22 [22, 32]
3-b	2.65	**3′**-b	3.13 [22, 32]
3-c	2.65	**3′**-c	–

[a] Letters a, b and c refer to the compounds with oxa-oxygen, thia-sulphur and selena-selenium, respectively.
[b] μ(CNDO/2) = 3.89, 3.73, 1.93 and 1.09 for **2**-a, **2′**-a, **2**-b or **2′**-b [26]; μ(MINDO/3) = 4.73 and 4.63 D for **2**-a and **2′**-b, respectively [26], and μ (ab initio) = 3.85 [26] or 3.58 D [27] for **2**-a.
[c] As calculated from the dipole moments of **1**-a, **1**-b or **1**-c, and of 2,2-dimethylbutanethione (2.26 D [29]) and 2,2-dimethylbutanone (2.71 D for ${}_{E}P + {}_{A}P = R_D$ [30]).
[d] From the dipole moments of 9(10H)-anthracen-9-one (**3**), thiobenzophenone (2.86 D [29]) and benzophenone (3.00 D [31]).

4H-thiopyran-4-one **2**-b, 9H-thioxanthen-9-one **3**-b, 9H-selenoxanthen-9-one **3**-c, 9H-xanthen-9-thione **3'**-a and 9H-thioxanthen-9-thione **3'**-b can be regarded as planar.

The σ-moment of both **2**-a and **3**-a can be equated to $\mu(\mathbf{1}\text{-a}) - \mu_\pi(C{=}O) = 1.75 - (\mu(H_2C{=}O) - \mu(Me{-}O)) = 1.75 - (2.34\,[21] - 1.12) = 1.75 - 1.22 = 0.53$ D, and that of **2'**-a and **3'**-a can be taken as $\mu(\mathbf{1}'\text{-a}) - \mu_\pi(C{=}S) = 1.30 - (1.65\,[21] - 1.13) = 1.30 - 0.52 = 0.78$ D. Similar calculations lead to $\mu_\sigma(\mathbf{2}\text{-b}) = \mu_\sigma(\mathbf{3}\text{-b}) = 1.50 - 1.22 = 0.28$ D, $\mu_\sigma(\mathbf{2}'\text{-b}) = \mu_\sigma(\mathbf{3}'\text{-b}) = 1.05 - 0.52 = 0.53$ D, and $\mu_\sigma(\mathbf{3}\text{-c}) = 1.67 - 1.22 = 0.45$ D. It follows that the π-moments of these compounds, $\mu_\pi = \mu - \mu_\sigma$, exhibit the values listed in Table 3, which can be compared with those calculated by quantum-mechanical techniques, if any.

2-a, **2'**-a, **2**-b and **2'**-b were examined by Zahradńik [40, 41] using the simple HMO technique, by Somogyi et al. [26] with the CNDO/2 method, and by Thomson and Edge [42] employing an ab initio technique. HMO calculations were made for **2**-a by Brown [43] and Beak [44], for **2**-a and **3**-a by Efimov and Komarov [45], and for **2**-a, **2**-b, **3**-a and **3**-b by Tolmachev, Dyadyusha and Shulezhko [46]. A self-consistent HMO technique ($\omega'\,\omega''\,\beta$) was applied to **2**-a by Hérault and Gayoso [47], then to **2**-a and **3**-a by Gayoso, Bouanani and Boucekkine [48]. More recently, ab initio methods were used for **2**-a by P. Császár et al. [26], and by Lumbroso, Pappalardo and Grassi [27].

Clearly, the HMO calculated π-moments for the ketones and thioketones listed in Table 3 are unrealistic, even though the values for **2**-a (5.5 D) and **3**-a (4.0 D) obtained by Gayoso et al. [48] using an improved HMO technique are not so much overestimated. The ab initio method affords too a high value, of 5.5 D [27]. Contrary to what is expected from theoretical calculations, the experimental π-moments of ketones **2**-a (3.17 D) and **2**-b (3.68 D) are close to those of the corresponding thioketones **2'**-a (3.30 D) and **2'**-b (3.88 D).

A comparison of the π-moments of the 4H-pyran-4-ones (**2**-a and **2**-b) and 4H-pyran-4-thiones (**2'**-a and **2'**-b) with those of the corresponding 9H-xanthen-9-ones (**3**-a and **3**-b) and 9H-xanthen-9-thiones (**3'**-a and **3'**-b) would be meaningful only if the appropriate π-moments lengths are taken into account: for instance, L(**2**-a) = 2.70 Å, L(**3**-a) = 1.91 Å, from [45]; L(**2**-a) = 2.10 Å, L(**3**-a) = 1,13 Å, following [48]; L(**2**-a) = 3.04 Å, L(**2'**-a) = 2.83 Å, L(**2**-b) = 2.95 Å, L(**2'**-b) = 3.34 Å, from [41]. This may explain the order observed for the π-moments of **2**-a and **3**-a, **2**-b and **3**-b, **2'**-a and **3'**-a, **2'**-b and **3'**-b (see Table 3). However, the chief cause of the π-moment differences is probably the (X...C=Y) interaction moment (defined just below), which nearly has the same length in **2**-a and **3**-a, **2**-b and **3**-b, and so forth.

2) 4H-pyran-4-ones (**2**-a and **2**-b) and 4H-pyran-4-thiones (**2'**-a and **2'**-b) are resonance hybrids of

Table 3. Calculated π-moments and interaction moments (M) of 4H-pyran-4-one, 9H-xanthen-9-one, and related compounds (Debye units).

Ketone	μ_π[a]	μ_π[b]	M[e]	R[f]	Thioketone	μ_π[a]	μ_π[e]	M[f]	R[f]
2-a	14.0, 12.0, 1.2, 12.2, 11.0, 5.5 and 5.5[b]	3.17	0.73	0.18	**2'**-a	9.9[g]	3.30	1.25	0.28
2-b	12.0, 13.8[c]	3.68	1.29	0.29	**2'**-b	11.7[g]	3.88	1.88	0.39
3-a	7.4, 4.0[d]	2.44	0.48	0.12	**3'**-a	–	2.44	0.87	0.19
3-b	–	2.37	0.32	0.07	**3'**-b	–	2.60	0.94	0.19
3-c	–	2.20	0.16	0.03	–	–	–	–	–

[a] Calculated by theoretical methods, see text.
[b] From the π-electron densities given in [43], [41], [47], [46], [45], [48], and [27], respectively.
[c] Cf. [41] and [46].
[d] See [45] and [48].
[e] From experimental dipole moments, see text.
[f] M (in Debye units) and R (in D/Å) are defined in text. The Y...Y distances (L in Angström units) used to calculate the R-values were taken from the microwave structures of **2**-a, **2'**-a and **2'**-b [5] (L = 4.07, 4.52 and 4.84), the X-ray structure of **3**-a [39] (L = 4.09); the values for **2**-b (4.39), **3**-b (4.41), **3'**-a (4.54), **3'**-b (4.86), and **3**-c (4.50), were readily deduced from those structures.
[g] From [41].

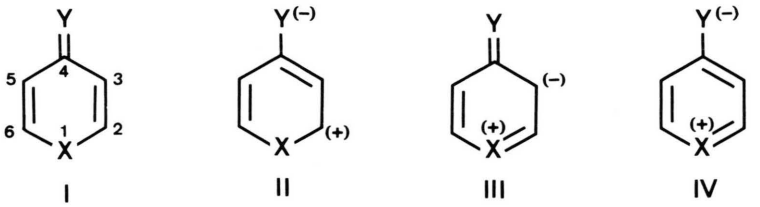

Fig. 1. Canonical structures for 4H-pyran-4-one **2**-a (X=O, Y=O), 4H-pyran-4-thione **2'**-a (X=O, Y=S), 4H-thiopyran-4-one **2**-b (X=S, Y=O), and 4H-thiopyran-4-thione **2'**-b (X=S, Y=S).

the valence structures I, II (two possibilities), III (two possibilities), and IV (two Kékulé and three Dewar formulae), shown in Figure 1. The interaction moment M originates from contribution of IV.

The dipole moment of compound **2**-b (3.96 D [28]) can be regarded as the algebraic sum of the following vectors:

μ(2,5-Cyclohexadien-1-one) = 4.07 D as calculated by the CNDO/2 method here giving a moment (4.46 D) close to that measured in benzene solution for similar 4,4-dimethyl-2,5-cyclohexadien-1-one (μ = 4.35 D) [49]. (The experimental dipole moment of 2,6-cycloheptadien-1-one is 4.04 D [49].)

$\Delta\mu$ = 0.24 D which measures the lack in additivity of aliphatic tetrahydrothio-4H-pyran-4-one (**1**-b).

μ(Thia-2,5-cyclohexadiene) = 1.64 D as equated to the dipole moment of octahydrothioxanthen (see [50]).

From these data it follows that the (S...C=O) interaction moment in **2**-b is calculated to be M(**2**-b) = 3.96 − (4.07 + 0.24 − 1.64) = 1.29 D.

Assuming μ(2.5-cyclohexadien-1-thione) = 4.07 + μ(Ph_2C=S) − μ(Ph_2C=O) = 3.93 D (see Table 2), M(**2'**-b) results as 4.41 − (3.93 + 0.24 − 1.64) = 1.88 D.

To calculate the interaction moments in **2**-a and **2'**-a, the dipole moment of oxa-2,5-cyclohexadiene is needed, for which a plausible value is obtained from the dipole moments of octahydrothioxanthen (1.64 D [50]) phenyl ether (1.15 D [51]) and phenyl thioether (1.55 D [52]), or from those of octahydrothioxanthen (1.64 D), xanthen (1.20 D [53]) and thioxanthen (1.32 D [53]), giving 1.24 and 1.52 D respectively; in the following μ(oxa-2,5-cyclohexadien) was taken as (1.24 + 1.52)/2 = 1.38 D.

M(**2**-a) is then calculated to be 3.70 − (4.07 + 0.28 − 1.38) = 0.73 D, and M(**2'**-a) to be 4.08 − (3.93 + 0.28 − 1.38) = 1.25 D.

Similar calculations can be performed for 9H-xanthen-9-one (**3**-a), 9H-xanthen-9-thione (**3'**-a), 9H-thioxanthen-9-one (**3**-b), 9H-thioxanthen-9-thione (**3'**-b) and 9H-selenoxanthen-9-one (**3**-c) (μ = 2.97, 3.22, 2.65, 3.13, and 2.65 D) from the dipole moments of 9(10H)-anthracen-9-one **3** (3.41 D) or 9H-anthracen-9-thione **3'** (3.27, see Table 2), xanthen (1.20 D) or thioxanthen (1.32 D), and selenoxanthen (1.32 D from μ (thioxanthen), μ(Ph_2Se) = 1.43 D [54] and μ(Ph_2S) = 1.55 D [52])*, leading to

M(**3**-a) = 2.97 − (3.41 + 0.28 − 1.20) = 0.48 D,
M(**3'**-a) = 3.22 − (3.27 + 0.28 − 1.20) = 0.87 D,
M(**3**-b) = 2.65 − (3.41 + 0.24 − 1.32) = 0.32 D,
M(**3'**-b) = 3.13 − (3.27 + 0.24 − 1.32) = 0.94 D,
M(**3**-c) = 2.65 − (3.41 + 0.28 − 1.20) = 0.16 D.

Existence of an interaction moment in **2**-a, **2'**-a, **2**-b, **2'**-b, and **3**-a, is supported by the theoretical calculations showing that a part (δ) of the oxa-oxygen or thia-sulphur $(np_z)^2$ lone-pair migrates as far as the carbonyl oxygen or thiocarbonyl sulphur. Thus (in electron units), δ(**2**-a) = 0.244 [43], 0.094 [41], 0.157 [46], 0.095 [45], and 0.025 [27]**; δ(**2'**-a) = 0.078 [41]; δ(**2**-b) = 0.200 [41]; δ(**2'**-b) = 0.174 [41], and δ(**3**-a) = nil [47] or 0.135 [48]. A considerable reduction in the carbonyl-bond multiplicity, due to contribution of (IV) for **2**-a or (IV') for **3**-a, is clearly indicated by their carbonyl oxygen-17 n.m.r. spectra [55],

Since the interaction moments are due to contribution of (IV) (or (IV')) which contain a benzene-like π-sextet (Figures 1 and 2), the M/(X...Y) ratio (R) is a significant measure of the aromaticity of the compounds quoted in Table 3.

That R(**3**-a) is inferior to R(**2**-a), and R(**3'**-a) is lower than R(**2'**-a), may be explained as follows. Contibutions of (IV) or (IV') to the actual electronic

* The dipole moments of xanthen, thioxanthen and diphenyl selenide were recalculated from Authors' data [53, 54], assuming ${}_EP + {}_AP = R_D$.

** Ab initio calculated π-densities for **2**-a are (in electron units), $q(1) = -0.2206$, $q(2) = q(6) = -0.0653$, $q(3) = q(5) = 0.0977$, $q(4) = -0.1739$, and $q(O) = 0.3297$, from [27]; see Fig. 1 for atom numbering.

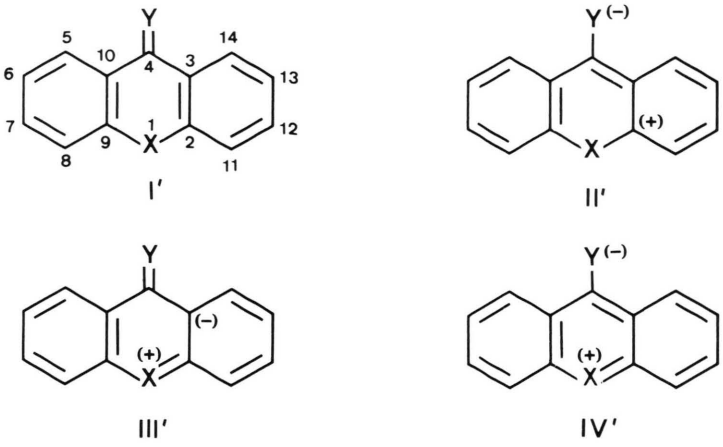

Fig. 2. Canonical structures for 9H-xanthen-9-one **3**-a (X=O, Y=O), 9H-xanthen-9-thione **3**′-a (X=O, Y=S), 9H-thioxanthen-9-one **3**-b (X=S, Y=O), 9H-thioxanthen-9-thione **3**′-b (X=S, Y=S). The structures with (+) at C_{12} and C_{14}, and those with (−) at C_{11} and C_{13}, are not represented.

structure of the molecules are determined by the energy needed to pass from (I) to (IV) or from (I′) to (IV′), in that the lesser is the energy needed, the higher is the contribution of the interaction valence structure (cf. [56, 57]). Since $E_\pi(\text{IV}') - E_\pi(\text{I}') = E_\pi(\text{IV}) - E_\pi(\text{I}) - E_R(\text{benzene}) + E_R(\text{4H-pyran-4-one})$, (IV′) should less contribute than does (IV) because in (IV′) one benzene-like π-sextet is replaced by a 4H-pyran-4-one π-sextet of lower resonance energy (see Fig. 2): $E_R = 1.6785\,\beta$ [46] as compared to $2.0000\,\beta$; Julg and François's aromaticity indices are 0.72 and 1.00 for 4H-pyran-4-one and benzene, respectively [58]. Likewise, R(**3**-b) is lower than R(**2**-b) and R(**3**′-b) smaller than R(**2**′-b) because the HMO-calculated resonance energy of 4H-thiopyran-4-one (**2**-b) is $1.6926\,\beta$ [46] and the experimental value (32.7 kcal mol^{-1} [59]) of 2,6-diphenyl-4H-thiopyran-4-one is markedly lower than that of benzene, 36 kcal mol^{-1} [4], both from combustion data. The small value of R(**3**-c) is less reliable than is R(**3**-b) since the dipole moment of selenoxanthen used has been estimated; it appears, however, of the same order of magnitude as the latter. Another possible explanation of all these observations is based on the fact that (IV) derives from (III) and (IV′) from (III′), whose contributions are related to the absolute π-charges at the C_3-atom in oxa- or -thia-2,5-cyclohexadiene, xanthen or thioxanthen, respectively. As the $(np_z)^2$ lone pair of oxa-oxygen or thia-sulphur migrates to C_3 (and C_5) in the former compounds and to C_3, C_{11} and C_{13} (and C_{10}, C_6 and C_8) in the latter (see Figs. 1 and 2 for atom numbering), it can be safely inferred that q_3 (in **3**-a and **3**′-a) is inferior to q_3 (in **2**-a and **2**′-a) and q_3 (in **3**-b and **3**′-b) is smaller than q_3 (in **2**-b and **2**′-b) (cf. [18]): q_3 (in **3**-a) = 0.0388 e as against q_3 (in **2**-a) 0.0724 e, from [35]. Note also that in (III′), and in (II′), one benzene sextet disappears.

The observation that R(**2**-b) is greater than R(**2**-a) and R(**2**′-b) higher than R(**2**′-a), both by 0.11 D/Å, was unexpected because, as indicated by the mesomeric moments (m) of thioanisole (0.40 D) and anisole (0.81 D) [60], q_3 (in modulum) should be smaller in thia-2,5-cyclohexadiene than in oxa-2,5-cyclohexadiene. A plausible explanation of these findings is that the mesomeric effect of thia-sulphur is more augmented than is the one of oxa-oxygen through interaction with an electron-withdrawing group; the $(\text{Y}\ldots p\text{-NO}_2)$ interaction moments are 0.62, 0.62 and 0.35 D (with $R = 0.16$, 0.17 or 0.10 D/Å) in p-nitroselenoanisole p-nitrothioanisole and p-nitroanisole, respectively. However, for the 9H-xanthen-9-ones, R(**3**-a) is slightly greater than R(**3**-b) by 0.05 D/Å, and R(**3**′-a) is equal to R(**3**′-b). This may be due to the fact that q_3 (in xanthen) is certainly much lower than q_3 (in oxa-2,5-cyclohexadiene) and q_3 (in thioxanthen) is inferior to q_3 (in thia-2,5-cyclohexadiene), this causing that the action of the carbonyl (or thiocarbonyl) group on the mesomeric effects of both thia-sulphur and oxa-oxygen is to be reduced. When competition occurs between the (X−phenyl) mesomeric effects, the mesomeric moments of Ph_2X, and the interaction moments of each $X-C_6H_4-NO_2$ moiety in $(p\text{-}NO_2C_6H_4)_2X$, little depend on the nature of the heteroatom X: $m(Ph_2Se) = 0.09$ D, $m(Ph_2S) = 0.06$ D, $m(Ph_2O) = 0.12$ D; m(thioxanthen) = 0.66 D, m(xanthen) = 0.44 D; $M(\text{S}\ldots p\text{-NO}_2) = 0.98$ D

($R = 0.26$) in 4-nitrophenyl phenyl thioether and $M(O\ldots p\text{-}NO_2) = 0.75$ D ($R = 0.21$) in *p*-nitrophenyl phenyl ether, $M(S\ldots p\text{-}NO_2) = 0.25$ D ($R = 0.07$) in di-(*p*-nitrophenyl) thioether, and $M(O\ldots p\text{-}NO_2)$ = nil or 0.19 D ($R = 0.05$) in di-(*p*-nitrophenyl) ether*. Interestingly, competition between the ($X\ldots p\text{-}NO_2$) interaction effects strongly lowers the interaction moments in these derivatives.

That the mesomeric effect of thia-sulphur is more increased than the one of oxa-oxygen through a positive π-charge induced by an electron-withdrawing substituent at the adjacent carbon atom may be accounted for by Coulson and de Heer's equation which relates the π-charge migration of the heteroatom (q) in a X-substituted unsaturated system, such as X−Ph, and thereby the mesomeric moment of X−Ph ($m = L \times q$), to the HMO LCAO parameters $k = \beta(C\text{---}X)/\beta(C\text{---}C)$ and $\tau = [\alpha(X) - \alpha(C)]/\beta(C\text{---}C)$ [71]; after these authors q varies as k^2/τ^3. As a consequence, a change in the τ-value leads to $\Delta m = KL \times (dq/d\tau) \times \Delta\tau = KL \times (3k^2/\tau^4) \times \Delta\tau$, where K designates a constant. It then follows that one may write

$$\frac{\Delta m'}{\Delta m''} = \frac{L' \times (3k'^2/\tau'^4)}{L'' \times (3k''^2/\tau''^4)} = (m'/m'') \cdot (\tau''/\tau') = (0.5) \cdot (\tau''/\tau'), \quad (1)$$

where k' and τ' refer to thioanisole and k'' and τ'' to anisole, whose experimental mesomeric moments are $m' = 0.40$ D and $m'' = 0.81$ D [60]. Now, for $(\tau''/\tau') = (2.0/1.0) = 2$ [40, 45], $\Delta m' = \Delta m''$, whilst for $\tau'' = 2$ and τ' small [72], $\Delta m'$ should be much greater than $\Delta m''$, for an equal change in the τ-value. However, when τ is small the charge migration (q) should vary as $k^2/(k^2 + \text{constant})$ [71]. Note also that, for $(\tau''/\tau') = 2$, $(m'/m'') = 0.5$ implies $(k'/k'') = 0.25$, a value which much differs from those [(0.8/0.6) or (1.0/0.8)] used in [41] and [46], respectively.

Since the contributions of (IV) and (IV′) are determined by those of (II) or (II′) [56, 57], and the thiocarbonyl group has a greater conjugation ability than the carbonyl bond in similar unsaturated ketones and thioketones [29, 73, 74], as expected R(**2**′-a) is higher than R(**2**-a), R(**2**′-b) is greater than R(**2**-b), R(**3**′-a) is superior to R(**3**-a) and R(**3**′-b) higher than R(**3**-b).

Conclusions

The R-values determined for 4H-pyran-4-one (**2**-a), 4H-pyran-4-thione (**2**′-a), 4H-thiopyran-4-one (**2**-b) and 4H-thiopyran-4-thione (**2**′-b) suggest the aromaticity order: (**2**-a) < (**2**′-a) ~ (**2**-b) < (**2**′-b) (Table 3), which compares well with that drawn from their ^{1}H n.m.r. spectra [75, 76]. The electronic spectra support an increased delocalization when passing from **2**-a to **2**′-a, **2**-b and **2**′-b [77]. The aromaticity index (A_I), which is a measure of the degree of averaging of the peripheral bonds in an aromatic skeleton, is 0.72 for 4H-pyran-4-one and 1.00 for benzene [58]. Balaban and Simon's index, based on the relative electrophilicity and nucleophilicity of a ring compared with that of benzene (taken as 0), is + 57 for 4H-pyran-4-one [78]. The carbonyl oxygen-17 of 4H-pyran-4-one is shielded by 101.8 p.p.m. compared to that of 2-cyclohexen-1-one, showing a high contribution of the (O...C=O) interaction valence structure (IV) in the former compound [55]. All these physico-chemical data, in our opinion, prove aromaticity for 4H-pyran-4-one, and its related compounds. By contrast, considerations of the molecular magnetic susceptibility of both 2H-pyran-2-one and 4H-pyran-4-one led to the conclusion that both are nonaromatic [79].

The R-values for 9H-xanthen-9-one (**3**-a), 9H-xanthen-9-thione (**3**′-a), 9H-thioxanthen-9-one (**3**-b) and 9H-thioxanthen-9-thione (**3**′-b) suggest the aromaticity order: (**3**-b) < (**3**-a) < (**3**′-a) ~ (**3**′-b) for their central ring. The carbonyl-oxygen basicities of (**3**-a), (**3**-b) and (**3**-c) follow the order (**3**-a) > (**3**-b) > (**3**-c) [16]. Gayoso and Ouamerali's new aromaticity index (based on the diamagnetic susceptibility exaltation), which is 49 for **3**-a and 92 for anthracen

* The relevant calculations were made with the following data: $m(Ph_2X) = \mu(Et_2X) - \mu(Ph_2X) = 1.27$ [51] − 1.15 [51] = 0.12 D for X=O, 1.61 [52] − 1.55 [61] = 0.06 D for X=S, and 1.52 [37] − 1.43 [54] = 0.09 D for X=Se, if conrotatory models are assumed for Ph_2X [54, 62]; m(xanthen) = $\mu(Et_2O) + \mu$(toluene) − μ(xanthen) = 1.27 [51] + 0.37 [63] − 1.20 [53] = 0.44 D, m(thioxanthen) = 1.61 [52] + 0.37 − 1.32 [53] = 0.66 D; $\mu(p\text{-}NO_2C_6H_4XMe) = 4.86$, 4.36 and 4.38 D [37] for X=O, S or Se; $\mu(PhNO_2) = 3.98$ D [64], μ(PhOMe) = 1.28 D acting at $\theta = 107°$ to the C_{ar}−O bond axis [65], μ(PhSMe) = 1.34 D with $\theta = 71°$ [60], μ(PhSeMe) = 1.31 D with $\theta = 72°$ [36]; $\mu(4\text{-}NO_2C_6H_4XC_6H_5) = 4.30$ D [66] for X=O and 4.26 D [67] for X=S; $\mu((p\text{-}NO_2C_6H_4)_2X) = 2.63$ D [66] or 2.83 D [68] for X=O, and 3.33 D [66] for X = S; $C_{ar}OC_{ar} = 123°$ [69], $C_{ar}SC_{ar} = 109.5°$ [70] .

[6], likely refers to the whole molecule, and not only (for **3**-a) to the central 4H-pyran-4-one ring. A noticeable contribution of the (O...C=O) interaction canonical structure (IV') for **3**-a is proved by the carbonyl oxygen-17 shift being 36.2 p.p.m lower than that of 9(10H)-anthracen-9-one [55]. Some aromaticity of the central ring of 9H-selenoxanthen-9-one (**3**-c) is not to be precluded.

We hope that the results here presented may be useful for further studies on the aromaticity of 4H-pyran-4-one and 9H-xanthen-9-one, and related compounds.

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