Thermochimica Acta, 177 (1991) 329–339
Elsevier Science Publishers B.V., Amsterdam

THERMOANALYTICAL INVESTIGATIONS ON HETEROCYCLIC ORGANIC COMPOUNDS.
Part VI. Synthesis, characterization and thermal decomposition of 1,4-bis(*p*-fluorobenzene sulphonyl)-2-alkoxy tetrahydropyrazines

SADIQ A. KANBER, ADIL H. IBRAHEIM and LAZGIN A. JAMIL

Department of Chemistry, College of Science, University of Salahuddin, Arbil (Iraq)

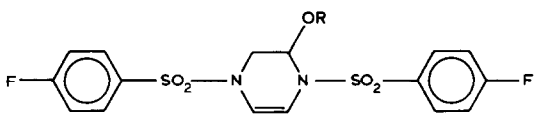
MAHMOOD M. BARBOOTI

Department of Chemical Industries, Petroleum Research Centre, Jadiriyah, P.O. Box 10039, Baghdad (Iraq)

(Received 7 March 1990; in final form 21 June 1990)

ABSTRACT

Seven derivatives of 1,4-bis(*p*-fluorobenzene sulphonyl)-2-alkoxytetrahydropyrazines with different alkoxy groups: amyl, *n*-butyl, 2-butyl, i-butyl, i-propyl, cyclopentyl and cyclohexyl are synthesized by reaction of 1,4-bis(*p*-fluorobenzenesulphonyl)-2,5-dihydroxypiperazine with the desired alcohol. The title compounds have the general structural formula:



The composition and structure were confirmed by elemental analysis, IR spectroscopy, NMR spectroscopy and mass spectral analysis. The thermal decomposition of these compounds occurs in three steps: removal of an alcohol, formation of *p*-fluorobenzenesulphonic acid or its anhydride and evolution of a tetrahydropyrazine ring. Finally, the sulphonic acid or anhydride deteriorates into carbon. Good correlation could be derived between the nature of the alkyl group and the decomposition temperature, with the branched and cycloalkyl derivatives requiring less energy to evolve the alcohol molecule, i.e. branching aids the decomposition.

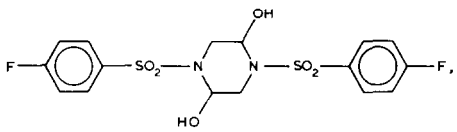
INTRODUCTION

The thermal analysis of heterocyclic organic compounds helps in establishing a correlation between thermal stability and composition [1], detection of reversible phase transformations [2] and derivation of new routes of decomposition, which may result in the preparation of special products [2,3].

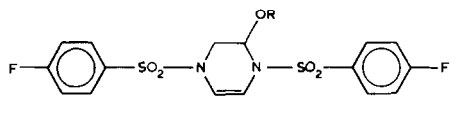
0040-6031/91/$03.50 © 1991 – Elsevier Science Publishers B.V.

The 1,3 dipolar cycloaddition of vinyl ether with sulphonylazide gives dialkoxy piperazines and dihydroxypiperazine A [4,5] which undergoes interconversion into C*i* [6]. Such compounds have biological activity [7] and can be used as monomers in polycondensation with bisphenol [8].

In the present paper, the synthesis of 1,4-bis(*p*-fluorobenzene sulphonyl)-2,5-dihydroxypiperazine, A, and its 2-alkoxy tetrahydropyrazines derivatives, C*i*, and their characterization by chemical analysis and spectral techniques are reported.



(A)



(Ci)

The thermal decomposition of the C*i* compounds is reported to establish relationships between structure and the decomposition process.

EXPERIMENTAL

Apparatus

The IR spectra were recorded for the KBr discs on a Pye–Unicam SP-1000 infrared spectrophotometer. The proton NMR spectral analyses were performed on a Varian EM-390 (90 MHz) NMR spectrometer using tetramethylsilane (TMS) as a standard. The thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were carried out on a Stanton–Redcroft TG 760 thermobalance equipped with a three-pen strip chart recorder under nitrogen gas flowing at a rate of 40 mL min^{-1}. Samples weighing 3–5 mg were heated in platinum pans at rates of 10, 20 and 30 °C min^{-1}. The elemental analyses and mass spectra were carried out at Alfred Bernhardt Laboratorien (F.R.G.).

Preparation of A

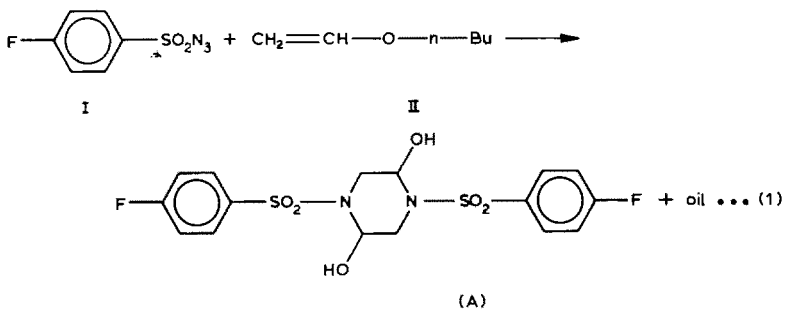
The *p*-fluorobenzene sulphonyl azide, **I**, which is prepared from the reaction of *p*-fluorobenzene sulphonyl chloride [9] with sodium azide [5], was added in very small portions to a large excess (50 ml) of *n*-butyl vinyl ether (Fluka), **II**, at room temperature. The white solid that formed was removed. The process was repeated five to seven times and the residual oil was separated. The characterization of this oil is dealt with in a separate work.

TABLE 1

Some physical data of compounds A, C*i*

No.	Compound	Recrystallization solvent (Melting point (°C))	Yield (%)	Chemical analysis [a]				
				C	H	N	S	F
C1	$C_{19}H_{20}N_2S_2O_5F_2$	CCl_4 (102–103)	85	49.77 (49.52	4.4 4.15	6.11 6.18	14.00 13.92	8.29 8.03)
C2	$C_{20}H_{22}N_2S_2O_5F_2$	CCl_4 (127–128)	90	50.84 (50.52	4.69 4.57	5.93 4.98	13.57 13.06	8.04 7.96)
C3	$C_{20}H_{22}N_2S_2O_5F_2$	CCl_4 (91–92)	85	50.84 (50.36	4.69 4.38	5.93 5.10	13.57 12.81	8.04 7.75)
C4	$C_{20}H_{22}N_2S_2O_5F_2$	$CHCl_3/CCl_4$ 1:1 (138–139)	85	50.84 (50.31	4.69 4.40	5.93 5.20	13.57 13.02	8.04 8.10)
C5	$C_{21}H_{24}N_2S_2O_5F_2$	$CHCl_3/CCl_4$ 3:1 (87–88)	85	51.84 (51.62	5.18 5.40	5.78 5.37	13.18 13.74	7.81 8.40)
C6	$C_{21}H_{22}N_2S_2O_5F_2$	P.E/CCl_4 1:1 (115)	88	52.06 (52.42	4.78 4.39	5.78 5.61	13.23 12.98	7.84 7.46)
C7	$C_{22}H_{24}N_2S_2O_5F_2$	P.E/CCl_4 1:1 (106)	86	53.00 (52.94	5.05 4.87	5.62 5.84	12.86 12.39	7.62 7.37)
A	$C_{16}H_{16}N_2S_2O_6F_2$	DMSO (147–148)	35	44.24 (44.63	3.70 3.62	6.45 6.19	14.76 14.57	8.75 8.17)

[a] Calculated values; experimental values in parentheses.



Preparation of the alkoxy tetrahydropyrazines

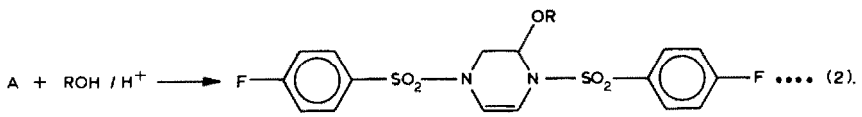
A mixture of about 2 mmoles of compound A and 20 ml of the desired alcohol was treated with two drops of hydrochloric acid and refluxed for 6–9 h. The reaction mixture was cooled, filtered and the precipitate recrystallized using specific solvent. The yield, chemical composition and melting points of the products are given in Table 1.

TABLE 2

The characteristic IR spectral data

Compounds	Wave number (cm^{-1})	Intensity [a]	Assignment
A	3480	sh, w	OH stretching
A, C	3110–3080	b, w	Aromatic C–H stretching
	2960–2880	b, w	Aliphatic C–H stretching
	1350–1340	sh, s	SO_2
	1180–1170	sh, s	SO_2
	1290–1270	sh, s	C–N
	1070–1030	sh, s	C–O–C
	970–960	sh, s	C–O–C
	900–890	sh, s	Ar–F
	840, 818	sh, s	Two adjacent H
	710, 675		Two adjacent H
	760	sh, m	Four adjacent H
C	1660–1650		C=C (THP ring)

[a] sh: sharp, w: weak, m: medium, b: broad, s: strong.



R = i-C_3H_7 (C1); *n*-C_4H_9 (C2); i-C_4H_9 (C3); 2-C_4H_9 (C4); *n*-C_5H_{11} (C5); cyclopentyl (C6); and cyclohexyl (C7).

RESULTS AND DISCUSSION

The structural features of compounds A and C1–C7 were determined by combining elemental analysis data (Table 1), IR spectral data (Table 2) and proton NMR data (Table 3). The IR spectra show a significant absorption peak at 3480 cm^{-1} which indicates the presence of an OH group in compound A and a peak at 1660 cm^{-1} which corresponds to the tetrahydropyrazine unit  .

The NMR data showed that the geminal methyl protons of the iso-propoxy group (compound C1) are characterized by well resolved signals at 0.93 and 0.68 ppm. Those of the iso-butoxy group (compound C3) were less well-resolved and occurred at 0.58 and 0.69 ppm. This suggests that the geminal methyl protons of compounds C1 and C3 are magnetically inequivalent, representing a case of diastereotropy as a result of the chirality of the

TABLE 3

Proton NMR data of compounds A, C*i* [a]

No.	C=C-Ha	C=C-Hb	H_2 equatorial, N-CH-O	H_3 equatorial	OH and O-CH-R	H_3 axial	CH_2 or CH	C-Me_1	C-Me_2	CH_3 solvent	NMR
C1	6.38(1H) d(7 Hz)	6.0(1H) d(7 Hz)	5.2(s,b) (1H)	3.9 (2H) (m) J = (14 Hz), 4 Hz		2.23(1H) 14 Hz		0.68(3H) d(6 Hz)	0.93(3H) d(6 Hz)		$CDCl_3$
C2	6.38(1H) d(6 Hz)	6.0(1H) d(6 Hz)	5.08(1H) (s,b)	3.95(1H) d(14 Hz)	3.4(2H) (m)	2.23(1H) d(14 Hz)	1.1(4H) (m)			0.8(3H) (m)	$CDCl_3$
C3	6.38(1H) d(6 Hz)	6.0(1H) d(6 Hz)	5.1(1H) (s,b)	3.95(1H) d(13 Hz)	3.2(1H) d(6 Hz)	2.28(1H) d(13 Hz)	1.4(1H) h(6 Hz)	0.58(3H) d(6.5 Hz)	0.69(3H) d(6.5 Hz)		$CDCl_3$
C4	6.4(1H) d(7 Hz)	5.9(1H) d(7 Hz)	5.15(1H) (s,b)	3.85 d(13 Hz)	3.2(2H) (m)	2.1(1H) d(13 Hz)	1.0(7H) (m)				$CDCl_3$
C5	6.35(1H) d(7 Hz)	5.95(1H) d(7 Hz)	5.1(1H) (s,b)	3.85(1H) d(12 Hz)	3.5(2H) (m)	2.2(1H) d(12 Hz)	1.65(6H) (m)			0.7(3H) (m)	$CDCl_3$
C6	6.38(1H) d(6 Hz)	5.9(1H) d(6 Hz)	5.13(1H) (s,b)	3.9(1H) d(15 Hz)	4.15(1H) (m)	2.23(1H) d(15 Hz)	1.4(8H) (m)				$CDCl_3$
C7	6.4(1H) d(7 Hz)	6.0(1H) d(7 Hz)	5.28(1H) (s,b)	3.95(1H) d(15 Hz)	3.6(1H) (m)	2.28(1H) d(15 Hz)	1.35(10H) (m)				$CDCl_3$
A			5.4(2H) (s,b)	3.65(2H) d(14 Hz)	6.2(2H) d(5.9 Hz)	3.1(2H) d(14 Hz)					DMSO-d_6

[a] The signals for the aromatics appear at 7.2 p.p.m. (m, 4H) and 7.8 p.p.m. (m, 4H); d = doublet, m = multiplet and h = heptet.

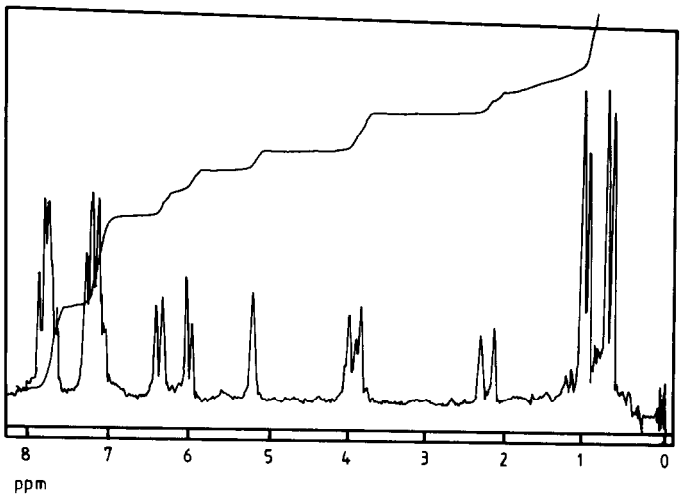


Fig. 1. Typical NMR spectrum of 1,4-bis(*p*-fluorobenzene sulphonyl)-2-alkoxy tetrahydropyrazines.

molecules [10]. Also, the occurrence of closely placed peaks (7.2 and 7.8 ppm) with an Ax Ax′ pattern in the aromatic region of the spectra for compounds A and C*i* suggests the inequivalence of the aryl group (Fig. 1).

Thermal decomposition studies

The TG and DTG curves of compounds C1–C7 are shown in Figs. 2–4. Three main decomposition steps characterized the thermal behaviour of these compounds. Resolution improved with lower heating rates. Only slight differences could be observed in the characteristic temperatures corresponding to the second and third steps, which can be accounted for by the formation of a common decomposition product at the end of the first step. The quantitative evaluation of the TG curves confirmed the removal of a tetrahydropiperazine ring  in the second step for all compounds. For the first step, the cyclic and branched alcohol C1, C3, C4, C6, and C7 derivatives gave strong evidence for the release of one alcohol molecule per molecule of the compound C*i*. The straight chain alcohol derivatives (C2 and C5) gave higher values of weight loss during the first decomposition step than if a simple alcohol was removed.

The DTA and DSC curves show that the three-step decomposition takes place immediately after the melting of the compounds. The first and second steps are exothermic, with overall features similar to the corresponding DTG peaks, while the third is endothermic, with a peak minimum at slightly higher temperature than the minimum of the corresponding DTG peak. The exothermic nature of steps 1 and 2 may indicate the formation of a

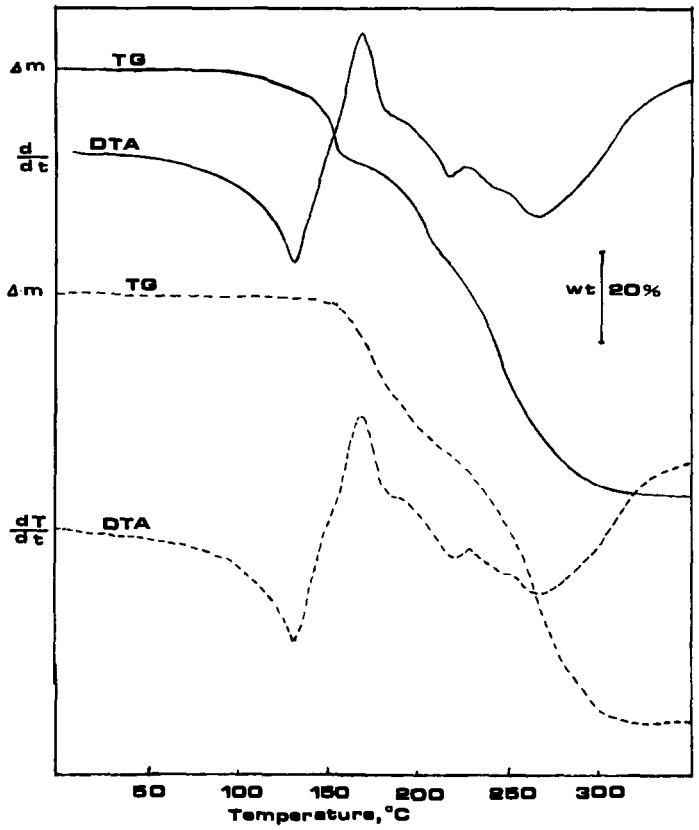
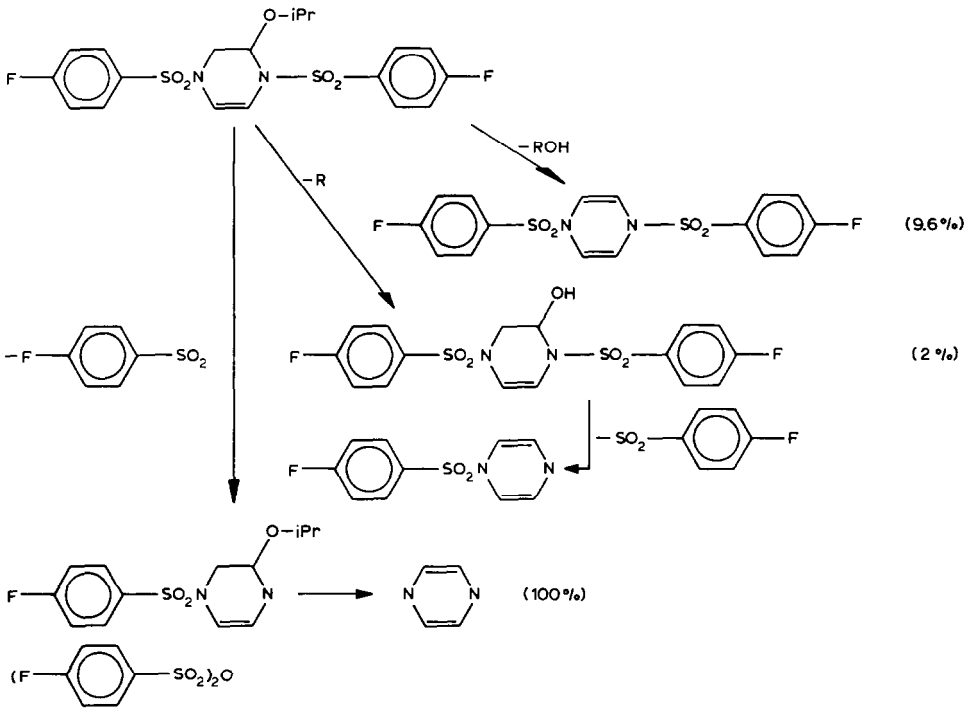


Fig. 2. TG and DTA curves of 1,4-bis(*p*-fluorobenzene sulphonyl)-2-isopropoxy tetrahydropyrazines (———) and 1,4-bis(*p*-fluorobenzene sulphonyl)-2-isobutoxy tetrahydropyrazines (------).

thermodynamically stable species, such as an alcohol, and the tetrahydropyrazine heterocycle, i.e. the bond formation energy exceeds the bond dissociation energy involved.

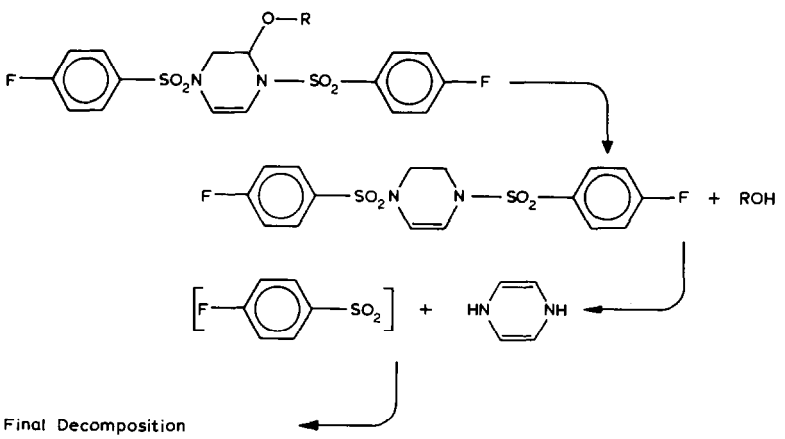
To account for the decomposition nature of the compounds, and the variation of weight losses for some compounds from the estimated values, a mass spectrum was recorded for the C1 (iso-propyl derivative). The spectrum indicates that fission of this compound leads to the formation of an alcohol (i-propyl alcohol), a tetrahydropyrazine and a *p*-fluorobenzenesulphonic acid and anhydride (Scheme 1). The spectrum also indicates the existence of other fragments with lower abundance, which gives the possibility of another route for thermal decomposition. Thus, the removal of alcohol followed by the rupture of the N–S bond to set free the tetrahydropyrazine ring, leaving the *p*-fluorobenzenesulphonic acid or anhydride, is a favoured route for the decomposition of C*i* compounds (Scheme 2).

The initial decomposition temperature and the peak maximum temperatures of alcohol removal were very much dependent on the type of alkyl



Scheme 1.

group attached to the oxygen in the alkoxy substituent (Table 4). From Table 4, the initial decomposition temperature of the compounds follows the order *n*-butyl > amyl > i-butyl > cyclopentyl > cyclohexyl > 2-butyl > i-propyl. The effect of branching is generally predominant in lowering the



Scheme 2.

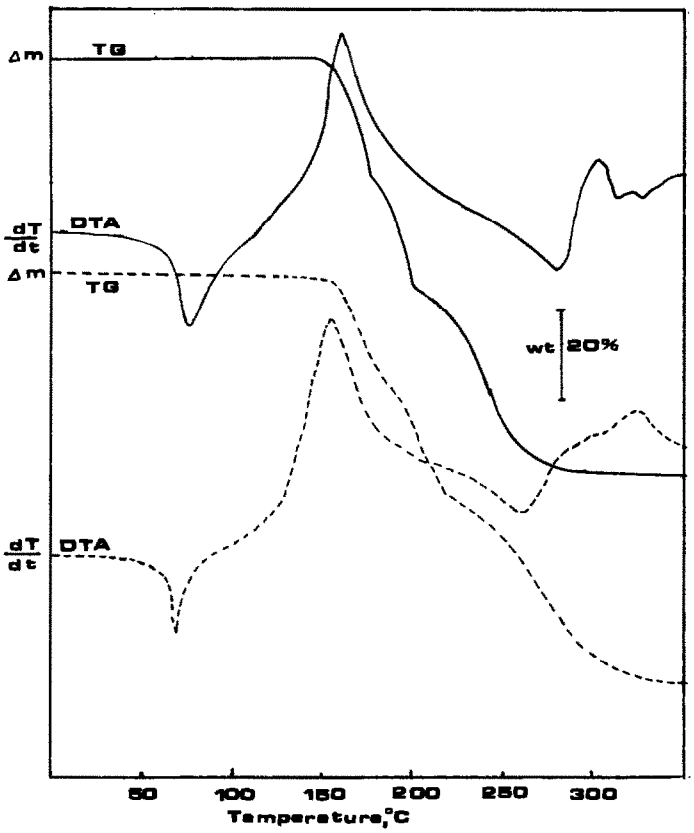


Fig. 3. TG and DTA curves of 1,4-bis(*p*-fluorobenzene sulphonyl)-2-(1-butoxy)tetrahydropyrazines (———) and 1,4-bis(*p*-fluorobenzene sulphonyl)-2-(1-pentoxy)tetrahydropyrazines (------).

decomposition temperature, aided by the steric hindrance of the bulky groups and long chain of the alkyl groups. The decomposition temperatures of the cyclo-derivatives within the branched alkyl derivatives support this explanation. The cyclohexyl derivatives appear to be less stable than the cyclopentyls, a behaviour which can be related to the difference in the relative stability of the corresponding alkoxy radicals. The cyclohexyl radical exists in chair and boat forms while the cyclopentyl radical exists only in chair form, i.e. the cyclohexyl radical is more stable than the cyclopentyl radical, making the formation of the latter energetically more difficult than that of the cyclohexyl radical. Furthermore, the existence of the cyclohexyl group in these two forms exerts more steric hindrance than does the cyclopentyl group, which occurs only as the boat form. The partial overlap of the first decomposition step for the amyl and *n*-butyl derivatives with the second steps accounts for the slight differences between the experimental weight loss values and the calculated values.

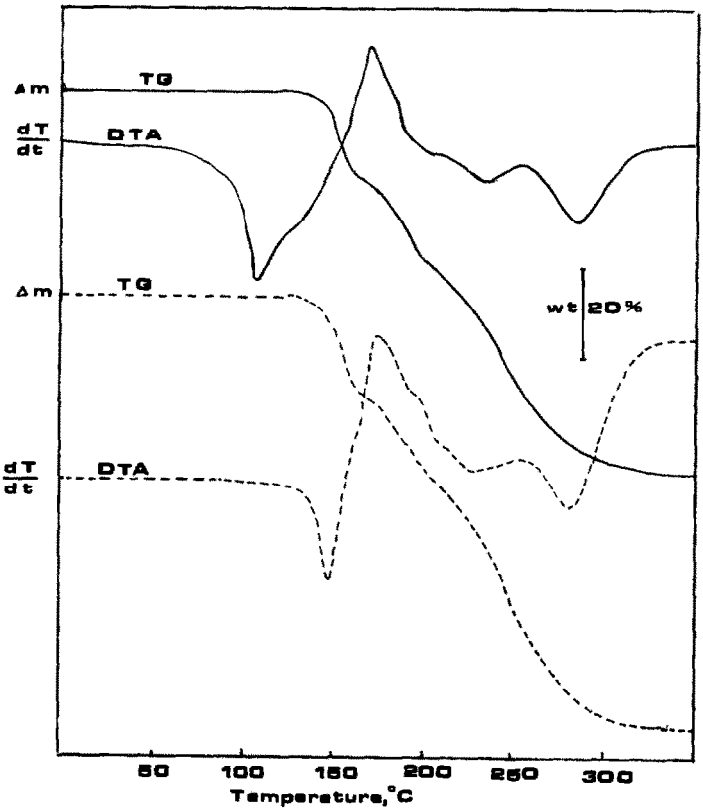


Fig. 4. TG and DTA curves of 1,4-bis(*p*-fluorobenzene sulphonyl)-2-cyclopentyloxy tetrahydropyrazines (———) and 1,4-bis(*p*-fluorobenzene sulphonyl)-2-cyclohexyloxy tetrahydropyrazines (------).

TABLE 4

The characteristic temperatures of the first decomposition reaction of 1,4-bis(*p*-fluorobenzenesulphonyl)-2-alkoxy tetrahydropyrazines

	Heating rate (°C min^{-1})					
	10		20		30	
Compound	T_i	T_{max}	T_i	T_{max}	T_i	T_{max}
Amyl	145	174	153	186	154	185
n-Butyl	152	177	155	181	156	183
2-Butyl	127	161	133	174	133	175
i-Butyl	140	162	144	171	145	170
i-Propyl	120	164	122	165	125	166
Cyclopentyl	136	160	145	169	145	170
Cyclohexyl	134	156	135	157	135	159

REFERENCES

1 H.T. Al-Badri and M.M. Barbooti, Thermochim. Acta, 53 (1982) 45.
2 M.M. Barbooti, H.T. Al-Badri and A.F. Roomaya, Thermochim. Acta, 70 (1983) 347.
3 H.T. Al-Badri, F. Abdul-Jalil and M.M. Barbooti, Thermochim. Acta 138 (1989) 13.
4 M.A.R. Khayate and S.A. Kanber, J. Iraqi Chem. Soc., 10 (1985) 54.
5 M.A.R. Khayate, S.M. Al-Araji, S.A. Kanber and S.H. Ridha, J. Iraqi Chem. Soc., 10 (1985) 39.
6 U. Eisner and A.J. Williams, J. Chem. Soc., Chem. Commun., 14 (1979) 606.
7 F.M. Ali, personal communication.
8 S.A. Kanber, unpublished data.
9 R.L. Shriner, R.C. Fuson, D.Y. Curin and M. Morrill, The Systematic Identification of Organic Compounds, Wiley, New York, 1980.
10 S.R. Salman, S.A. Kanber and M.A.R. Khayate, Can. J. Spectrosc., 32 (1987) 115.