TABLE I

Band head data of the new $A^2\Pi-X^2\Sigma$ and $B^2\Sigma-X^2\Sigma$ systems of the SrI molecule

Wavenumber (cm⁻¹)	Assignment		$\nu_{obs.} - \nu_{cal.}$ (cm⁻¹)
	v', v''	System	
14085	0, 2	A_1	+3·6
14256	0, 1	A_1	+0·2
14428	0, 0	A_1	0
14579	0, 1	A_2	+0·2
14597	1, 2	A_2	+1·4
14616	1, 0	A_1	−1·0
14643	0, 0	B	0
14752	0, 0	A_2	0
14769	1, 1	A_2	+1·2
14804	2, 0	A_1	−1·0
14818	1, 0	B	0
	3, 1	A_1	−0·8
14941	1, 0	A_2	0
14956	2, 1	A_2	+0·2
14992	2, 0	B	0
15129	2, 0	A_2	0
15143	3, 1	A_2	+0·2

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LEUCOPELARGONIDIN FROM HYDNOCARPUS WIGHTIANA

THE powdered pericarp of *H. wightiana* was defatted with petroleum ether and extracted completely with cold acetone. The acetone extract was concentrated to a thick syrup at low pressure and extracted with ether and then with ethyl acetate.

The ethyl acetate extract was dried and concentrated to a thick orange-red liquid under reduced pressure. Gradual addition of petroleum ether (40-60) removed the coloured impurities and then gave a light brown solid. This was redissolved in small quantity of dry ethyl acetate and fractionally precipitated with petroleum ether (40-60), followed by cooling, until a colourless powder (4·5 g) was obtained.[1] It did not melt till 300° C but darkened at 218-225° C with spurting. (Found : C, 54·7; H, 5·6; $C_{15}H_{14}O_6$, 2 H_2O requires C, 55·3; H, 5·4). It gave a bluish-green colour with ferric chloride and a pink colour with alco-

holic hydrochloric acid which deepened on heating.

The compound was converted into anthocyanidin chloride as described for leucodelphinidin chloride.[1] The 1% hydrochloric acid solution gave the following : (a) a positive ferric reaction, (b) almost completely extracted with cyanidin reagent, (c) no change on air oxidation, (d) Rf. (circular, phenol-water lower layer) 0·88. The ethonolic hydrochloride solution had absorption maximum at 535 mμ.

The leucoanthocyanidin formed a colourless penta-acetate with acetic anhydride and pyridine in the cold. It softened at 161° C and melted at 168-169° C. (Found : C, 59·6, H, 5·1 ; $C_{25}H_{24}O_{11}$ requires C, 60 ; H, 4·8%.) The trimethyl ether of the leucoanthocyanidin was prepared using ethereal diazomethane ; crystallised from methanol and melted at 146-149° C. (Found : C, 65·1 ; H, 6·5 ; $C_{18}H_{20}O_6$ requires C, 65 ; H, 6·1%.) On acetylation, the methyl ether gave the diacetate, m.p. 180-183° C (Found : C, 63·3 ; H, 5·6 ; $C_{22}H_{24}O_8$ requires C, 63·4 ; H, 5·8%) and on oxidation with powdered potassium permanganate[1] gave an acid, m.p. 181-183° C, which was identified as anisic acid by m.m.p. and co-chromatogram with authentic sample.

From the above observations, the leucoanthocyanidin, isolated, has been identified as leucopelargonidin.

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STRUCTURE OF NO₂⁻

NO_2^- with 19 valence electrons is isoelectronic with O_3^-, ClO_2 and SO_2^-. Following the arguments of Walsh,[1] we would expect the 19-electron AB_2 systems to be bent in the ground state with an apex angle between 110° and 120°. We have now carried out CNDO/2 calculations[2] on NO_2^- and O_3^- to find the bond distances and angles in their electronic ground states. In addition, we have calculated the normal vibrations in NO_2^- and compared the calculated and observed infrared frequencies.

In our CNDO/2 calculations, we have minimized the energy of the system with respect to the bond distance and the bond angle. In

the case of NO_2^- we obtained a bond angle of 118·5° and an N-O distance of 1·23 Å; the observed apex angle[3-5] in NO_2^- is 115·4°. The results of our calculations on $NO_2^=$ and O_3^- are listed along with the results of NO_2 and NO_2^- in Table I. We see that the calculated apex

lated the vibrational modes of $NO_2^=$ in order to substantiate the assignments and to obtain some information on the structure. For this purpose we employed the Urey-Bradley-Shimanouchi Force Field.[7] We assumed the N-O distance of 1·30 Å and a reasonable ONO angle[5]

TABLE I

CNDO/2 calculations on AB_2 systems

Molecule	No. of valence electrons	Angle, deg.		r, Å		μ, D		Charges	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Central atom	End atom
NO_2	.. 17	137·7	132·0	1·20	1·20	0·74	± ·4	+0·410	−0·205
NO_2^-	.. 18	118·5	115·4	1·23	1·236	2·81	..	+0·088	−0·544
$NO_2^=$	.. 19	123·0	..	1·30	..	4·26	..	−0·338	−0·831
O_3^-	.. 19	118·5	..	1·20	..	3·20	..	+0·083	−0·541

angle in $NO_2^=$ is larger than expected while the N-O distance is exactly what one would have expected.[5] The N-O bond order in $NO_2^=$ is considerably lower than in NO_2 or NO_2^-; the negative charges on both N and O atoms increase in the series NO_2, NO_2^- and $NO_2^=$. In the case of O_3^-, the calculated bond distance is shorter than expected while the apex angle is higher.[5]

We note here that there should be a decrease in the bond angle while going from an 18-electron AB_2 system to a 19-electron system although the magnitude of the decrease may be smaller than that associated with a change from a 16- to a 17-electron system.[1] Our calculated angles for both $NO_2^=$ and O_3^-, however, do not show this trend. It is possible that bond angles calculated for open shell systems like $NO_2^=$ and O_3^- are not reliable. In order to obtain more information regarding the structure of $NO_2^=$ we next examined its vibrational spectrum.

The infrared spectrum of freshly prepared Na_2NO_2 exhibits three bands at 1298, 1238 and 880 cm^{-1} which can be assigned to the ν_{asym} (NO_2), ν_{sym} (NO_2) and δ(ONO) modes respectively. These observed frequencies of $NO_2^=$ fall in line with the observed frequencies of NO_2 and NO_2^- (Table II). We calcu-

of 110° and fixed the N-O stretching force constant, $K_{(NO)}$, by making use of the plot of $K_{(NO)}$ of NO_2, NO_2^-, NO ($B^2\Delta$) and NO ($B^2\pi$) against the N-O bond distance.[8] We applied a 3% correction for anharmonicity for all these force constants.[9] The $K_{(NO)}$ thus obtained for $NO_2^=$ was 6·40 m dynes/Å. We iterated the bending and 1-3 interaction force constants[10] and could obtain a good fit for the observed frequencies when $H_{(CNO)} = 0·45$ and $F(O---O)$ 1·85 m dynes/Å, etc. We could not obtain any reasonable fit of frequencies with a $K_{(NO)}$ of 6·40 when the bond angle was 120°. It appears that a bond angle of 110° and an N-O distance of 1·30 Å appropriate for $NO_2^=$.

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TABLE II

Fundamental frequencies of NO_2, NO_2^- and $NO_2^=$

	ν_{asym} (NO_2) cm^{-1}	ν_{sym} (NO_2) cm^{-1}	δ (ONO) cm^{-1}	Ref.
NO_2 (obs.)	.. 1618	1320	750	6
NO_2^- (obs.)	.. 1328	1201	828	4
$NO_2^=$ (obs.)	.. 1298	1238	880	Present study
$NO_2^=$ (calc.)	.. 1299	1214	880	,,

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