1002. *The Intensity of Ultraviolet-light Absorption by Monocrystals. Part IV.* Absorption by Naphthacene of Plane-polarized Light.*

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Measurements on the intensity of light absorption in naphthacene are reported and used to determine the polarizations of four electronic transitions. The experimental results are compared with the predictions of recent theories of the electronic states of the molecule. General agreement between theory and experiment exists for systems I, III, and IV but there is some uncertainty about system II.

In previous work on the naphthacene crystal spectrum a photoconductance method [1] was used, as well as more conventional methods.[2,3] Borisov's work [2] was quantitative, but the strongest bands were not measured, nor was absorption at energies greater than 38,800 cm.$^{-1}$. The present work, done before Borisov's results were available, extends his measurements and is used to test various theories [4-7] of the electronic states of the naphthacene molecule. Eichis [8] recorded the dispersion curve in the region of the long-wave system and deduced the reduced oscillator strengths $f_b = 0{\cdot}07$ and $f_a = 0{\cdot}03$, parallel and perpendicular to the *b* axis respectively. (We define f_b by the relation $f_a = 1{\cdot}44 \times 10^{-9}\int\varepsilon_b d\nu$.) We know of no other determination of oscillator strength.

No detailed information on the crystal structure of naphthacene has yet been published.

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* Part III, *J.*, 1959, 1551.

[1] Bree and Lyons, *J. Chem. Phys.*, 1954, **22**, 1630.

[2] Borisov, *Trudy Inst. Fiz. Akad. Nauk Ukr. S.S.R.*, 1953, **4**, 102; Technical translation TT-613 N.R.C., Ottawa, 1956 (by G. Belkov); *Izvest. Akad. Nauk S.S.S.R.*, 1953, **17**, 689.

[3] Craig, Hobbins, and Walsh, *J. Chem. Phys.*, 1954, **22**, 1616; Sidman, *ibid.*, 1956, **25**, 122.

[4] Klevens and Platt, *J. Chem. Phys.*, 1949, **17**, 470.

[5] Moffitt, *J. Chem. Phys.*, 1954, **22**, 320.

[6] Ham and Rudenberg, *J. Chem. Phys.*, 1956, **25**, 13.

[7] Pariser, *J. Chem. Phys.*, 1956, **24**, 250.

[8] Eichis, *Trudy Inst. Fiz., Akad. Nauk Ukrain., S.S.R.*, 1954, **5**, 137; *Chem. Abs.*, 1955, **49**, 5130b.

An early analysis[9] showed that naphthacene crystals are triclinic, with only a very small departure from the monoclinic class. The crystal belongs to the space group $P\bar{1}$ and the unit cell has the symmetry S_2. Crystals grown by sublimation were flakes with the (001) as the developed face. A more recent study[10] of the crystal and molecular structure by Sinclair was kindly made available through Professor D. P. Craig. An investigation of Sinclair's structure by J. R. Walsh showed that the in-plane molecular axes were not orthogonal and that if the two available sets of naphthacene unit-cell parameters[9,10] were used to calculate the crystal density[11] very poor agreement between the calculated cell volumes was reached. A new determination of the density was therefore carried out. Naphthacene crystals were suspended in alcohol–chloroform, and the relative solvent concentrations varied until a naphthacene crystal remained suspended for several hours approximately mid-way between the upper and the lower liquid surfaces well away from the walls of the containing vessel. From the measured density of the liquid the crystal density was found to be $1{\cdot}29 \pm 0{\cdot}01$ g./c.c. This agrees quite well with the unit-cell volume calculated from the earlier data[9] (estimated density = 1·293 g./c.c.) but not so well with Sinclair's data[10] (estimated density = 1·25 g./c.c.), but the latter will be used here to compare the crystal and solution spectra, since no other information is available.

In triclinic crystals there are no necessary relations amongst the molecular axes, the crystal axes, the absorption axes (defined in ref. 12), and the principal axes of the indicatrix. The molecular and crystal axes have been related by Sinclair. The extinction directions of the sublimation flake in the visible region of the spectrum were used in the present work as the reference directions in the crystal. Relations were needed, therefore, between extinction and absorption directions in the flake, and between extinction directions and molecular axes.

It has been assumed, following Robertson,[13] that the crystal and optical properties of naphthacene are very similar to those of anthracene and naphthalene. Some evidence which supports this assumption is (i) that the conoscopic interference patterns of sublimation flakes of naphthalene, anthracene, and naphthacene show, in the extinction positions, a single isogyre which sweeps rapidly across the field of view, (ii) that the slow direction of the section is normal to the trace of the optic axial plane, (iii) that all crystals possess a negative birefringence, and (iv) that angles between crystal edges show that the developed crystal faces (001), (201), and (110) are the same for anthracene[14] and naphthacene.[9] Thus it is to be expected that a principal axis of the indicatrix will be close to the *b* crystal axis. The *b* crystal axis was tentatively identified on a few well-formed naphthacene flakes by measuring some angles between crystal edges. The angles measured were 124° and 104° which were associated respectively with the angles between the normals to the (110) and (201) faces and between the normals to the (110) and $(1\bar{1}0)$ faces. The *b* crystal axis was given as the trace of the (201) plane on the (001) plane.

The slow extinction direction of the flake in the visible was within 2° of the *b* crystal axis as found above, and thus these two directions coincide within the experimental error when the crystal is aligned in the polarized incident light. This behaviour again parallels that observed in anthracene where the slow extinction direction coincides with the *b* crystal axis.

The experiments were carried out with the electric vector of the plane-polarized light vibrating along an absorption direction of the sublimation flake. The absorption directions at 2300 Å were located by experiment: the crystal was rotated about an axis parallel to the incident light beam until maximum absorption in the slow direction was obtained. The rotation (12° at 2300 Å) was neglected in predicting the crystal spectrum from the

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[9] Hertel and Bergk, *Z. phys. Chem.*, 1936, **33**, *B*, 319.

[10] Sinclair, Ph.D. Thesis, Glasgow, 1955.

[11] Walsh, personal communication.

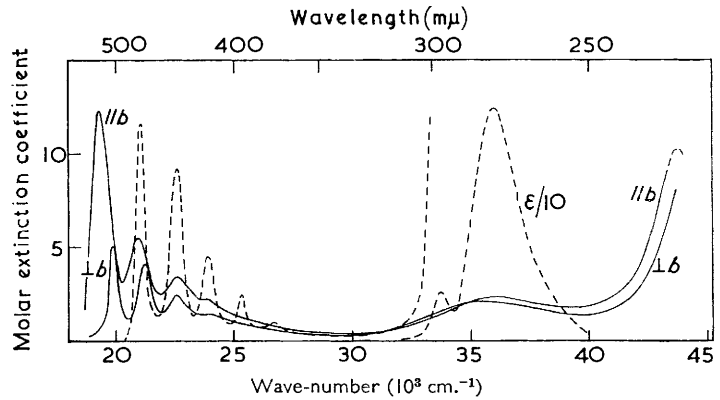
[12] Hartshorne and Stuart, " Crystals and the Polarizing Microscope," Arnold, London, 1950.

[13] Robertson, " Organic Crystals and Molecules," Cornell Univ. Press, New York, 1950.

[14] Winchell, " Optical Properties of Organic Compounds," Academic Press, New York, 1954.

solution spectrum but the error so introduced was not significant. It is therefore assumed that the crystal axes are related to the absorption directions of the naphthacene sublimation flake in the following way: the *p* direction is normal to the *ab* plane and the *q* direction lies in the *ab* plane normal to the *b* axis; *b* is then assumed to be the slow direction and *q* the fast direction of the sublimation flakes examined.

Absorption Spectrum.—The absorptions of three naphthacene monocrystals were measured, and the crystal thicknesses were estimated (i) by measuring their retardations with the aid of the Ehringhaus compensator at the sodium-D line and in white light, and (ii) by observing transmission interference effects in the visible and the near infrared region. The error in the absorption measurements was expected to be about 5% at wavelengths greater than 2500 Å, since all readings except the *b* absorption at 5200 Å fell in the optical density range less than 1. This 5200 Å absorption is liable to a small and probably negligible correction for stray-light errors. The observed retardations of the crystals are proportional to the optical densities in one polarization at any wavelength. The observed correspondence was excellent and confirmed that the error in the absorption measurements was indeed less than 5%. However, to convert the optical density readings into extinction coefficients, the thickness and density of the sample must be known.



To convert an optical thickness into a physical thickness, information on refractive indices is required. The smaller refractive index of the indicatrix section in the plane of the sublimation flake was determined to be 1·72 ± 0·01 at the sodium-D line. The estimation was made by means of the Becke immersion test, methylene iodide–α-chloronaphthalene mixtures being used as the immersion liquid. The larger refractive index in the section was too high to be measured with the immersion media available. With this information, the crystal thicknesses were found from the transmission interference spectrogram measured with the plane of the polarized light normal to the *b* axis. This was possible as the crystal was sufficiently thin to obviate any ambiguity in the order of interference. Once the crystal thicknesses were known, the refractive index of the second extinction direction in the crystal section was found. The birefringence in sodium light was 0·194.

The error in the crystal-thickness determination, assessed at about 5%, was calculated from the spread about the mean of the individual thickness estimates from the interference maxima and minima. Reflection losses were expected to reduce the calculated extinction coefficients by about 6%. It was not considered important to measure reflection losses in this case, since other accumulated errors in the absorption measurements totalled 10%.

Details of the naphthacene spectra are shown in the Figure, and Tables 1 and 2. The extinction coefficient quoted for the *b* polarized peak at 5200 Å was obtained with the thinnest crystal.

TABLE 1. *Molar extinction coefficients at the turning points of system I in naphthacene.*

λ (Å)	ν (cm.$^{-1}$)	$\varepsilon_{obs.}$	λ (Å)	ν (cm.$^{-1}$)	Polarization	ε′ calc. for $A_{1g} - B_{2u}$	ε′ calc. for $A_{1g} - B_{1u}$	$\varepsilon_{obs.}$	$\varepsilon_b/\varepsilon_q$	Band-pass (cm.$^{-1}$)	Borisov's ε values
4740	21,100	11,600	5200 ± 5	19,230 ± 20	*b*	150	26,700	12,300	2·41	15	
			5035 ± 5	19,860 ± 20	*q*	2340	5300	5100			7300
4580	21,830	1250	4930 ± 7	20,280 ± 30	*b*	16	2880	3100		16	4740
			4880 ± 10	20,490 ± 40	*q*	252	570	1100		16	1970
4450	22,470	9200	4775 ± 10	20,940 ± 40	*b*	120	21,200	5500	1·34	20	7900
			4715 ± 5	21,210 ± 20	*q*	1860	4200	4100		20	6330
4290	23,310	1250	4570 ± 15	21,880 ± 70	*b*	16	2880	2400		25	3720
			4555 ± 10	21,950 ± 40	*q*	252	570	1400		25	3520
4170	23,980	4500	4440 ± 10	22,500 ± 40	*b*	60	10,400	3350	1·39	35	4700
			4425 ± 10	22,590 ± 40	*q*	910	2050	2400		35	3890
3950	25,320	2500	4200 ± 15	23,710 ± 70	*b*	32	5700	2200	1·57	50	
			4180 ± 15	23,920 ± 70	*q*	500	1140	1400		50	1900

TABLE 2. *Naphthacene. Molar extinction coefficients in systems* II, III, *and* IV.

(a) *Calculated on the assumption that the factor group splitting is small so that contributions from the α- and β-crystal components to the absorptions along the b and q directions are combined (see Table* 5).

(b) *Calculated on the assumptions* (i) *that the factor group splitting is large*[c] *so that the α- and β-crystal components of each molecular absorption band do not overlap, and* (ii) *that the α-component is displaced to a much higher energy region.*

	Solution			Crystal								
	λ (Å)	ν (cm.$^{-1}$)	ε	λ (Å)	ν (cm.$^{-1}$)	Polarization	ε′ calc. for $A_{1g} - B_{1u}$	ε′ calc. for $A_{1g} - B_{2u}$	ε′ calc. for $A_{1g} - B_{3u}$	$\varepsilon_{obs.}$	Band pass (cm.$^{-1}$)	Borisov's ε values
II	2960	33,780	25,400[d]	2770 ±30	36,100 ±400	*b*	58,300[a]	5280[a]	12,600[a]	2400	160	5640
						q	11,900[a]	6200[a]	58,200[a]	2000	150	3660
III	2775	36,000	124,000[d]	2800 ±30	35,700 ±400	*b*	284,000[a]	220[b]	61,000[a]			
						q	58,000[a]	890[b]	284,000[a]			
IV	2270	44,100	17,000[e]	2290 ±40	43,800 ±1500	*b*	39,000[a]	3500[a]	8400[a]	10,000	700	
						q	7950[a]	4150[b]	39,000[a]	>8000		

[c] Craig and Hobbins, *J.*, 1955, 539, 2309. [d] Ref. 15. [e] Ref. 4.

TABLE 3. *Comparison of oscillator strengths in solution and crystal for naphthacene. The f′ values are oscillator strengths for the crystal estimated from the solution spectrum by using first-order perturbation theory and assuming z polarization for systems* I *and* II.

	System I					System		System
n	0	1	2	3	Total	II	III	IV
f_b	0·017	0·0090	0·0064	0·0028	0·041	0·023		0·036
f'_b	0·022	0·020	0·015	0·010	0·084	0·08	0·001 *	
f_q	0·0041	0·0047	0·0042	0·0020	0·019	0·020		
f'_q	0·0045	0·0056	0·0031	0·0020	0·017	0·02	(0·11) †	
$f_{soln.}$	0·029	0·036	0·020	0·013	0·11	0·11	1·37	0·09 (to cut off)
f_b/f_q	4·1	1·9	1·5	1·4	2·2			

* Only the β-component was considered, system III being assumed *y*-polarized. † Expected at higher energies.

The solution spectrum of naphthacene (Figure) was measured in oxygen-free benzene under nitrogen. System I was recorded by using a " Unicam " spectrophotometer fitted with a glass prism; the agreement of this spectrum with that reported by Clar [15] was excellent. System II was reproduced from Clar's spectrum.

[15] Simpson and Peterson, *J. Chem. Phys.*, 1957, **26**, 593.

Discussion of the Naphthacene Spectrum.—The naphthacene absorption spectrum is seen to reproduce the general behaviour already observed with anthracene. System I is *b* polarized, and the polarization ratio (b/q) is, as with anthracene, less than the oriented gas model prediction of 5/1 (see Table 1). The intensity of system III is apparently very much reduced in going from solution to the crystal, and system IV appears at the lower-wavelength limit of the observations.

Because of the low symmetry exhibited by naphthacene crystals, the two molecules in the unit cell will not transform one into the other by reflection through a glide plane or by rotation about a screw axis. For this reason, transition moments involving either an α or β crystal level are expected to have projections along all three absorption directions associated with the (001) plane. Thus, the crystal transition moments are not confined either to the *ac* plane or to the *b* axis, but each has components along the *b*, *q*, and *p* directions.

The intensities of crystal absorptions (given as the squares of the projections of the crystal transition moments, on the usual oriented gas-model assumptions) are shown in Table 4.

TABLE 4. *Naphthacene: Intensities of the crystal transitions which arise from unit transition moments along the molecular axes* [(*m.q*) *denotes the sum of the cosines of the angles between a given molecular axis and the q crystal direction*].

	α-Crystal component			β-Crystal component			α- and β-Components combined		
Molecular axis	$(m.q)^2$	$(m.b)^2$	$(m.p)^2$	$(m.q)^2$	$(m.b)^2$	$(m.p)^2$	$(m.q)^2$	$(m.b)^2$	$(m.p)^2$
Short	0·0018	0·766	0·059	0·154	0·0004	0·019	0·156	0·766	0·078
Long	0·078	0·068	0·854	0·0024	0·0006	0·0013	0·081	0·069	0·856
Normal	0·767	0·0007	0·0594	0·0002	0·164	0·0087	0·767	0·165	0·068

System I can be explained in terms of a molecular transition to a B_{1u} upper state. In this case a transition to any one crystal level is largely confined to a single absorption direction (see Table 4). This prediction agrees well with the observed spectrum; *e.g.*, there is no shoulder in the *q* polarized absorption curve at 5200 Å, *i.e.*, 19,230 cm.$^{-1}$.

System II may be seen clearly in the solution spectrum of naphthacene (Figure) as a smaller peak on the red side of the strong absorption of system III. It might be thought that this peak could be attributed to excitation of a ground-state vibrational mode of frequency 2200 cm.$^{-1}$ and belonging to system III; but the general shape of the absorption, especially in comparison with the shape of the corresponding anthracene solution spectrum, suggests that this is not the correct explanation. This conclusion is confirmed by a consideration of the intensity of the band. The extinction coefficient of the assumed "hot" band calculated by using Boltzmann statistics would be about 10. The likely alternative is that the peak marks a separate electronic transition. The quantities which characterize the solution absorption at 33,800 cm.$^{-1}$ are $\varepsilon_{\text{soln.}} = 25{,}400$ and $f_{\text{soln.}} = 0{\cdot}11$, but the estimated oscillator strength and, to a smaller extent the extinction coefficient, are in error because of the overlying stronger absorption at slightly higher energy. There is another source of error in comparing actual and calculated extinction coefficients arising from the flat nature of the absorption bands in the crystals. Projections along the absorption directions *b* and *q* of the 33,800 cm.$^{-1}$ band in solution are given in Table 2, it being assumed that the transition is polarized along each of the three molecular axes in turn. The 33,800 cm.$^{-1}$ solution band must provide α- and/or β-crystal components to the crystal absorption in much the same wavelength region. From the values in Table 2, both B_{1u} and B_{3u} symmetries seem to be excluded. The molecular transition is therefore described as $A_{1g} \longrightarrow B_{2u}$ polarized along the *y* axis although the observed intensity is rather greater than expected. It is not easy to see the explanation of this absorption in the light of the existing theories of molecular levels (cf. Table 5). If it marks a ^1L_b upper state it is at too high an energy. If, however, it marks a ${}^1B_{1u}{}^+$ state, the polarization has been reversed.

Consideration of oscillator strengths, however, allows either a B_{1u} or a B_{2u} assignment if an out-of-plane transition is excluded for other reasons.

The explanation of system III in the crystal which has been given by Simpson and Peterson[15] would account for some of the intensity in the crystal which in the previous paragraphs has been considered as arising from system II. The intensity from system III would appear chiefly in the *a* polarization. There is no resultant clarity in the assignment of system II, which is therefore left in doubt.

System III in the molecule is very intense and is the analogue of the strongest absorption system in anthracene. In the naphthacene crystal the absorption between 30,000 and 40,000 cm.$^{-1}$ is much weaker than would be expected for the α and β components of system III, and in part at least must be explained as arising from system II. Even if contributions from system II were completely neglected, the assignment of system II to a $A_g \longrightarrow B_{1u}$ transition would be impossible to reconcile with the appearance of either the α- or the β-crystal component in the region 30,000—40,000 cm.$^{-1}$. If the α-component were present, ε_b' would be 284,000; if the β-component were present, ε_q' would be 57,000. Both greatly exceed the observed result. In a similar way the assignment $A_g \longrightarrow B_{3u}$ may be excluded.

The assignment of system III to a $A_g \longrightarrow B_{2u}$ transition also leads to difficulty unless the α-component is assumed removed to lower wavelengths and the β-component alone remains in the region 30,000—40,000 cm.$^{-1}$. Such a removal of the α-component has been observed in the case of anthracene[16,17] and has been predicted for the naphthacene crystal.[18] For the B_{2u} assignment the values of ε_q' and ε_b' (Table 2) are quite small and can therefore easily be reconciled with experiment.

It follows that system III is definitely to be assigned to a $A_{1g} \longrightarrow B_{2u}$ transition and that a second case has been found experimentally of a factor-group splitting of at least several thousand cm.$^{-1}$. The sense of the observed splitting, the β-component lying at the lower energy, is also in accord both with the experiments on anthracene and with theory. The actual location of the β-components is difficult owing to the very low intensity, but in any case more refined theory leads to a more complicated distribution of intensity than just having two isolated components (cf. ref. 15).

Only the onset was studied of the crystal absorption which marks system IV. An absorption leak in *b* polarization was located at 43,800 cm.$^{-1}$ but the extinction coefficient value quoted (10,000) has probably been reduced by stray light and by the extreme width of the slit (2 mm.). The extinction coefficient of the corresponding peak in the solution spectrum is 17,000. By taking projections on to the *b* axis of the three possible molecular transition-moment directions in turn, it is seen that only one of the three gives $\varepsilon_b' = 10{,}000$. This is for the shorter in-plane molecular axis (upper-state symmetry B_{1u}) for which $\varepsilon_b' = 39{,}000$. System IV in solution appears as three rather broad peaks, and the oscillator strength for this entire system is 0·28.[4] Presumably the crystal band at 43,800 cm.$^{-1}$ is the first of the three. The oscillator thrength of the first solution peak was estimated roughly (because of the difficulty in separating the three vibrational peaks) as 0·09. A B_{1u} upper-state symmetry being assumed, the projection on the *b* axis is 0·069, which agrees moderately well with the observed value 0·036. For B_{3u} and B_{2u} upper states, the f_b' estimates are 0·015 and 0·0004, respectively. Thus it may be concluded than system IV, because of its intensity, probably arises from an electronically allowed transition to a B_{1u} upper state.

Thus the absorptions in crystals of anthracene and naphthacene may be given very similar interpretations. System I marks an allowed transition to a B_{1u} upper state and

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[16] Bree and Lyons, Part II, *J.*, 1956, 2662.

[17] Lyons and Morris, *J.*, 1959 1551.

[18] Craig and Walsh, unpublished work.

the strongest system arises from an allowed $A_{1g} \longrightarrow B_{2u}$ (long axis polarized) transition. For both crystals, evidence has been found of an electronic transition which occurs near to the very strong system; in naphthacene this transition, II, is probably to a B_{2u} upper state.

The spectral dependence of the photocurrent in single crystals of naphthacene with plane-polarized incident light has been shown to reproduce the polarized absorption spectrum [1] in the region of the first transition. The magnitude of the photocurrent in the spectral dependence curve was very nearly proportional to the molar extinction coefficient of the absorption spectrum, so that the correspondence was almost quantitative. From the spectral dependence of the photocurrents at higher energies it was previously [1] concluded that there were peaks in the absorption spectrum at 35,700 and 43,100 cm.$^{-1}$, in each case the light polarized parallel to the *b* direction being more strongly absorbed. These conclusions are now seen to be correct, and the usefulness of the photocurrent method vindicated in this instance at least.

The observed and calculated spectral properties in naphthacene are summarised in Table 5. Systems I and III show clear agreement in all cases. System IV shows agreement between experiment and the calculations both of Pariser and of Ham and Rudenberg. Agreement is possible also with the Klevens and Platt's assignment if the transition is made allowed by an appropriate vibration. System II is doubtful, but on the whole the modern theories have been successful in predicting the polarization properties of the transitions.

TABLE 5. *Observed spectral properties of naphthacene compared with theoretical results.*

System	Obsd. in solution		Obsd. in crystal				Moffitt [a]	Pariser [b]			Klevens and Platt [c]	Ham and Rudenberg [d]		
	ev	f	pol.	ev	f_a	f_b	f (calc.)	Assignment	f (calc.)	ev (calc.)	Assignment	Assignment	ev (calc.)	f (calc.)
I	2·6	0·11	z	2·4	0·2	0·04	0·10	z $^1B_{1u}{}^+$	0·44	3·1	z ^1L_a	z ^1L_a	3·07	0·8
	buried			buried?			0·002				y ^1L_b	y ^1L_b	3·06	0·03
II	4·2	0·10	y or z	4·5	0·02	<0·02		z $^1B_{1u}{}^+$	0·16	4·7		z ^1L_a		
III	4·5	1·37	y	4·5(b)	?	<0·02	2·16	y $^1B_{2u}{}^+$	3·78	5·1	y ^1B_b	y ^1B_b	4·9	3·97
IV	5·4	0·09 [e] (to cut off)	z	5·6	?	0·04		z $^1B_{1u}{}^+$	0·00	6·5	forb. ^1C_b	z ^1B_a	5·4	0·75
V	5·9	0·45						z $^1B_{1u}{}^+$	1·20	6·9	z ^1B_a	^1L_b		
VI	6·9	0·27						y $^1B_{2u}{}^+$	0·09	7·2	^1C_a			

[a] Ref. 5. [b] Ref. 7. [c] Ref. 4. [d] Ref. 6. [e] Total $f_{\text{soln.}} = 0·28$.

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