239. *The Electrical Moments of* p-*Benzoquinone and Related Compounds.*

By D. Ll. Hammick, G. C. Hampson, and G. I. Jenkins.

p-Benzoquinone as ordinarily formulated is sufficiently symmetrical to be non-polar, yet it appears to be slightly, but definitely, polar. It has been shown that not only this compound, but also its symmetrical dimethyl- and dichloro-derivatives, and 2 : 2 : 4 : 4-tetramethyl*cyclo*butane-1 : 3-dione, all have about equal differences between their total and electron polarisations. A mechanical model of the classical structure of *p*-benzoquinone bends very easily in such a way as to bring the two carbonyl groups out of the plane of the ring, and it seemed possible that the polarisations might arise from slow bending in this mode, due to thermal energy, which would enable the molecule to orient as a dipole while bent. It is concluded that such bending cannot be important, for if it were, the polarisations of the other diketones should be markedly different, which is not the case, and the rigidity of the ring is attributed to resonance. Furthermore a calculation of the frequency of this kind of bending does not agree with the infra-red absorption frequency. Both frequencies are far too high for orientation to occur, so the thermal bending theory is excluded and the polarisation discrepancies are considered either to be rather high atom polarisations, in agreement with the measurements in the far infra-red, or solute–solvent interactions.

A determination of the electric dipole moment of *p*-benzoquinone by Hassel and Naeshagen (*Z. physikal. Chem.*, 1930, *B*, **6**, 441), by measurement of the total and the electron polarisation at one temperature, gave the value of 0·67 D. in benzene solution (D. = 10^{-18} e.s.u.). Since *p*-quinone is usually assigned a symmetrical planar structure (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106), which should have zero moment, a further investigation of this anomaly was undertaken. Hassel and Naeshagen's value was confirmed and work was extended to similar compounds and to solvents other than benzene (Hammick, Hampson, and Jenkins, *Nature*, 1935, **136**, 990).

On the assumption that the atom polarisation in *p*-quinone is small, the observed difference between total and electron polarisation may be explained by postulating a non-rigid structure for the molecule, and the construction of a mechanical model indicated that the molecule was not nearly as rigid as the graphic formula would lead one to expect. If the quinonoid structure can be easily distorted by simultaneous rotation about the four single bonds, then, as will be shown later, the moment of 2 : 5-dimethyl-*p*-benzoquinone should be slightly larger and that of the 2 : 5-dichloro-compound appreciably less than that of *p*-benzoquinone. The flexibility theory was further tested by measuring the moment of 2 : 2 : 4 : 4-tetramethyl*cyclo*butane-1 : 3-dione, where, owing to the large strain already present in the four-membered ring, a further distortion of the molecule by thermal impacts is improbable.

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene. B.D.H. AnalaR benzene was frozen out three times to remove homologues and then refluxed over phosphoric oxide in a stream of dry air for 1 hour. Finally it was distilled in an all-glass apparatus into a receiver, protected from moisture by the dry air stream.

Carbon tetrachloride. Albright and Wilson's pure material for medicinal purposes was refluxed over phosphoric oxide and then distilled in a dry air stream.

n-Hexane. B.D.H. pure hexane for spectroscopy was used without further purification. It was dried in the same manner as benzene.

p-Benzoquinone. The material used for the measurement in benzene was obtained from crude quinol according to "Organic Syntheses," **2**, p. 85. Purification was effected by crystallising it twice from benzene; m. p. 113·3—113·8°. For measurements in carbon tetrachloride and *n*-hexane the quinol was crystallised from water before oxidation to *p*-quinone. The crude quinone was steam-distilled, then crystallised once from benzene and twice from benzene–ligroin (b. p. 60—80°); m. p. 112·8—113·6°. The m. p. is lower than that of most workers (Hesse, *Annalen*, 1860, **114**, 300, gives 115·7°), but careful purification by crystallisation and sublimation gave no further change.

2 : 5-Dimethyl-1 : 4-benzoquinone. This was prepared from *p*-xylidine (redistilled, b. p. 213—215°) by oxidation with potassium dichromate (Kehrmann and Stiller, *Ber.*, 1912, **45**, 3348). The mixture was steam-distilled and extracted with ether. The solid was crystallised twice from alcohol and finally sublimed in a vacuum; m. p. 123·6—124·3°. Carstanjen (*J. pr. chem.*, 1881, **23**, 423) gives 123·6°; Nietzki (*Ber.*, 1880, **13**, 472) gives 125°.

2 : 5-Dichloro-1 : 4-benzoquinone. Quinol was chlorinated directly with hydrochloric acid and potassium perchlorate to 2 : 5-dichloroquinol, which was then oxidised with sodium dichromate (Ling, J., 1892, **61**, 558). The product was crystallised once from alcohol, once from benzene, and sublimed in a vacuum; m. p. 160·4—161·4°. Ling (*loc. cit.*) gives 161°, Levy and Schultz (*Annalen*, 1881, **210**, 150) 159°, and Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 1484) 161°.

2 : 5-Dibromo-1 : 4-benzoquinone. This was prepared from quinol by direct bromination in glacial acetic acid with bromine, followed by oxidation with ferric chloride at 50° for 2 hours (Sarauw, *Annalen*, 1881, **209**, 113). The crude product was crystallised once from alcohol and twice from benzene. It was sublimed in a vacuum immediately before measurement; m. p. 190·6—191·3°. Sarauw (*loc. cit.*) gives 188°.

2 : 2 : 4 : 4-Tetramethyl*cyclo*butane-1 : 3-dione. The first sample was prepared from α-bromo*iso*butyryl bromide and freshly coppered zinc turnings, in a stream of dry nitrogen (Wedekind, *Ber.*, 1906, **39**, 1644; Staudinger and Klever, *ibid.*, p. 968). Distillation of the ligroin extracts yielded, at 75—90°/60 mm., a quantity of oil in which crystals were embedded. These were freed from the oil by filtration and purified by sublimation at reduced pressure. The yield was very poor; m. p. 113·3—114·3°.

For satisfactory purification and for accurate measurement a larger amount of the substance than was given by the above method is required. Very good yields were obtained by the action of dry triethylamine on pure *iso*butyryl chloride (Wedekind and Weiswange, *Ber.*, 1906, **39**, 1631). The reaction was carried out in dry carbon disulphide in an atmosphere of dry nitrogen. The combined carbon disulphide–ether extracts were fractionated at 40—50 mm.; the distillate at 90—100° condensed to a mixture of oil and solid material. The solid, separated by filtration, was washed several times with ice-cold ligroin. The total yield from three experiments (8·6 g. from 75 g. of *iso*butyryl chloride) was crystallised twice from ligroin (b. p. 80—100°) and fractionally sublimed at 200 mm.; m. p. 113·7—114·0°.

Measurements.—The approximate solution method developed by Debye ("Polar Molecules," New York, 1929, p. 42) was used for the evaluation of the total polarisation of the compounds, with a heterodyne-beat apparatus. The solution condenser was constructed of brass plated with platinum (H. O. Jenkins and Sutton, J., 1935, 609). Refractive indices were measured in a centrally divided cell on a Pulfrich refractometer, the source of light being a filtered mercury arc. Densities were measured in an ordinary Sprengel–Ostwald type pyknometer of about 10 c.c. capacity.

Tables of Results.

f_2.	$d_{4^\circ}^{t^\circ}$.	ϵ.	n^2.	P_2.	$_EP_2$.
		p-Benzoquinone in benzene at 25°.			
0·029697	0·8833	2·2934	2·2605	37·36	28·60
0·023679	0·8818	2·2898	2·2600	37·21	28·21
0·017521	0·8796	2·2852	2·2593	37·20	28·36
0·010103	0·8773	2·2799	2·2583	36·81	28·11
0·0	0·8739	2·2727	2·2571	—	—

$_{A+O}P_2 = 37{\cdot}15 - 28{\cdot}32 = 8{\cdot}83$ c.c.; $\mu = 0{\cdot}65$D.

f_2.	$d^{t°}_{4°}$.	ϵ.	n^2.	P_2.	$_EP_2$.
p-Benzoquinone in carbon tetrachloride at 25°.					
0·021117	1·5767	2·2409	2·1373	37·72	28·55
0·016292	1·5785	2·2378	2·1362	38·01	28·47
0·012396	1·5800	2·2349	2·1352	37·80	28·24
0·007794	1·5817	2·2320	2·1339	38·52	—
0·0	1·5847	2·2263	2·1329	—	—
$_{A+O}P_2 = 38·01 - 28·42 = 9·59$ c.c.; $\mu = 0·68$D.					
p-Benzoquinone in *n*-hexane at 40°.					
0·00657	0·6530	1·8685	—	35·56	—
0·00610	0·6527	1·8684	—	37·61	—
0·00605	0·6525	1·8680	—	37·01	—
0·00589	0·6526	1·8684	—	37·98	—
0·0	0·6502	1·8841	—	—	—
$_{A+O}P_2 = 37·0 - 28·4 = 8·7$ c.c.; $\mu = 0·66$D.					
2 : 5-Dimethyl-1 : 4-benzoquinone in benzene at 25°.					
0·030880	0·8831	2·2955	2·2603	47·89	38·19
0·021684	0·8803	2·2886	2·2597	47·81	38·40
0·014363	0·8780	2·2833	2·2588	47·92	38·46
0·009585	0·8766	2·2796	2·2583	47·65	38·43
0·0	0·8737	2·2727	2·2571	—	—
$_{A+O}P_2 = 47·8 - 38·4 = 9·5$ c.c.; $\mu = 0·68$D.					
2 : 5-Dichloro-1 : 4-benzoquinone in benzene at 25°.					
0·020514	0·8917	2·2921	2·2640	47·38	38·17
0·018770	0·8903	2·2900	2·2645	46·87	38·91
0·016542	0·8882	2·2881	2·2629	47·29	38·49
0·013273	0·8857	2·2885	2·2618	47·08	37·78
0·008273	0·8810	2·2804	2·2610	47·23	38·62
0·0	0·8737	2·2727	2·2571	—	—
$_{A+O}P_2 = 47·2 - 38·4 = 8·8$ c.c.; $\mu = 0·64$D.					
2 : 5-Dibromo-1 : 4-benzoquinone in benzene at 25°.					
0·00776	0·8878	2·2829	—	54	—
0·0	0·8737	2·2727	—	—	—
$_{A+O}P_2 = 54 - 44·0$ (calc.) $= 10$ c.c.; $\mu = 0·70$D.					
2 : 2 : 4 : 4-Tetramethyl*cyclo*butane-1 : 3-dione in benzene at 25°.					
1st measurement :					
0·01192	0·8748	2·2760	2·2492	49·0	35·1
0·00737	0·8744	2·2748	2·2538	49·1	38·8
0·00492	0·8742	2·2731	2·2538	45·9	35·5
0·0	0·8737	2·2727	2·2571	—	—
$_{A+O}P_2 = 48 - 36 = 12$ c.c.; $\mu = 0·8$D.					
2nd measurement :					
0·02778	0·8763	2·2792	2·2459	48·57	38·53
0·02062	0·8757	2·2779	2·2483	48·66	38·09
0·01438	0·8751	2·2760	2·2503	48·37	37·50
0·00856	0·8746	2·2748	2·2526	48·50	36·58
0·0	0·8738	2·2727	2·2571	—	—
$_{A+O}P_2 = 48·5 - 37·7 = 10·8$ c.c.; $\mu = 0·72$D.					

Prof. J. Errera and Dr. C. H. Cartwright very kindly measured the refractive indices of a solution of *p*-benzoquinone in benzene, in the far infra-red. They reported as follows : " The following measurements and calculations refer to a solution of 2·5 g. of *p*-benzoquinone in 20 c.c. of benzene. R is the percentage reflection, n the index of refraction, $T_{\text{meas.}}$ the transmission actually measured, $T'_{\text{corr.}}$ is the transmission corrected for reflection (quartz–liquid and liquid–quartz), and n_a is the absorption coefficient as calculated from $T' = e^{-4\pi nad/\lambda}$, where d is the thickness of the solution.

λ in μ	52	63	83	100	117	152
γ in cm.$^{-1}$	192	159	120	100	85	66
R meas. for soln., %	3·9	3·9	4·0	4·6	4·5	4·4
R for pure benzene, %	3·9	3·9	3·8	3·9	4·0	4·0
n of solution	1·49	1·49	1·50	1·54	1·54	1·53
n for pure benzene	1·49	1·49	1·49	1·49	1·50	1·50
$T_{\text{meas.}}$ for $d = 0·50$ mm., %	59·3	52·5	10·0	33·2	54·0	61·2
$T'_{\text{corr.}}$, %	64·4	57·0	10·8	35·3	57·4	65·1
$n_a \times 10^3$ for soln.	3·5	5·6	29·5	16·6	10·3	10·4
$n \times 10^3$ for benzene	1·0	1·3	2·4	3·8	4·5	5·7

The decided absorption band near 120 cm.$^{-1}$ is the most clearly defined of any we have observed from studying 25 liquids. There is also considerable evidence to indicate that this band is due to a fundamental mode of vibration of the entire molecule (such as a bending)."

Other data for the solution :

Molecular fraction, f_2, = 0·0935; density (at 16·5°) = 0·9124; refractive index in far infra-red (n_{ir}) = 1·53 to 1·52. $_{\text{E.+A}}P_1$ (benzene) = 25·6 c.c. (Cartwright and Errera, *Proc. Roy. Soc.*, 1936, *A*, **154**, 138).

From these data $_{\text{E+A}}P_2$ (*p*-benzoquinone) = 44·5 c.c. (for n_{ir} = 1·53) to 37·9 c.c. (for n_{ir} = 1·52). Taking $_{\text{E}}P_2$ as 28·3 c.c. from previous data (*vide supra*), it follows that the atom polarisation of *p*-benzoquinone, $_{\text{A}}P_2$, is 16·2 to 9·5 c.c.

DISCUSSION.

The experimental results are summarised in the following table :

Substance.	Solvent.	P_2.	$_{\text{E}}P_2$.	$_{\text{A+O}}P_2$.	%.	μ.
p-Benzoquinone	C_6H_6	37·15	28·32	8·83	31·2	0·65
,, ...	CCl_4	38·01	28·42	9·59	33·8	0·68
,, ...	*n*-C_6H_{14}	37·0	28·4	8·7	30·6	0·66
Dimethylquinone	C_6H_6	47·8	38·4	9·5	24·8	0·68
Dichloroquinone	,,	47·2	38·4	8·8	22·9	0·64
Dibromoquinone	,,	54	44·0	10	22·7	0·70
Tetramethyl*cyclo*butanedione............	,,	48·5	37·7	10·8	28·6	0·72

The remeasurement of the electrical polarisations of *p*-benzoquinone confirmed the value obtained by Hassel and Naeshagen and by Le Fèvre and Le Fèvre (J., 1935, 1696). All the compounds measured have geometrically symmetrical molecules whose electrical moments should be zero, yet the observed differences between the total and the electron polarisations in solution are from 8·6 to 10·8 c.c. The possibility of polar impurities being present can be ruled out, since different specimens prepared or purified by different methods gave identical results. As regards solvent effect, the values for *p*-quinone in benzene, carbon tetrachloride, and *n*-hexane are identical within the experimental error, and so if the moment is to be attributed to a solvent effect, it cannot be a specific effect of one solvent. The anomalous electrical moments can therefore be ascribed to one of three causes—atom polarisation, a flexibility moment due to a non-rigid nature of the molecule, or a general solvent effect.

The question of atom polarisation is dealt with more fully in the following paper. The value of this quantity, as obtained from vapour measurements, was usually of the order of 4 c.c. and very rarely exceeded 6 c.c. (Sugden, *Trans. Faraday Soc.*, 1934, 738), so it seemed improbable that the value in *p*-benzoquinone and its derivatives would be as large as 9 c.c. The usual allowance for atom polarisation is 5—10% of the electron polarisation (Wolf and Fuchs, " Dielektrische Polarisation," Leipzig, 1935, pp. 262, 299; Groves and Sugden, J., 1935, 971; 1937, 1779), but in these compounds the proportion would be much greater, ranging from 22% for the dichloroquinone to 34% for *p*-benzoquinone in carbon tetrachloride solution.

That the anomalous moment may be due to a flexibility of the molecule was suggested in an earlier communication (Hammick, Hampson, and Jenkins, *loc. cit.*). Le Fèvre and Le Fèvre (*loc. cit.*) also have made this suggestion. From the constancy of the polarisation with temperature they deduce that the real moment is zero, but the range of temperature employed (25° to 45°) is too small to warrant such a deduction.

The flexibility of the quinonoid structure is indicated in Figs. 1 and 2. A mechanical model showed that the plane formed by carbon atoms 2, 3, 5 and 6 was rigid, but those formed by 1, 2 and 6 and by 3, 4 and 5 were capable of oscillating about *ab* and *cd*, respectively, as axes. Over a certain small range the oscillation was fairly free from any retarding force, but outside this range considerable pressure was necessary to distort the molecule further. When the carbon atoms (1, 2 and 6) forming the plane *ABC* are deflected to the position *A'BC*, it is assumed that the entire strain is taken up by the change of angle α to ϕ, the amount of the strain being $\alpha - \phi$. With this assumption it follows that $\cos\phi = \cos\alpha \cdot \cos\theta$; $\alpha = 125°15'$ in the quinone molecule. The graph of $\alpha - \phi$ against θ shows that over a small range of θ the strain set up is small but then increases rapidly. Assuming that the observed dipole moment of *p*-quinone is entirely due to such a thermal oscillation and that the individual moment of the C=O link is 2·5 D., it follows that a *permanent* deflection (θ) of 8° ($\sin^{-1}$ 0·66/5·0) is sufficient to produce the moment. A deflection of 8° produces a strain of 24′ per carbon atom (calculated from the above equation). The energy increase required to produce this is 1·2 cals. per g.-mol. (Sidgwick, *Ann. Reports*, 1932, 65) or for the whole molecule, *i.e.*, four strained links, 4·8 cals. As the average energy of impact at 25° is 600 cals. per g.-mol., the flexibility of the molecule can easily be accounted for by thermal impacts. The observed polarisations are indeed much smaller than one would expect to be produced by the thermal energy of 600 cals., but Pauling and Sherman (*J. Chem. Phys.*, 1933, **1**, 614) calculate that the resonance energy of *p*-benzoquinone is approximately 13,000 cals., which they attribute to large contributions from resonance forms having benzenoid rings. These structures would stiffen the molecule appreciably, so the low values of the moments do not necessarily constitute an objection to this theory.

FIG. 1.

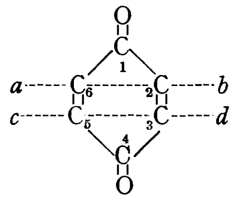
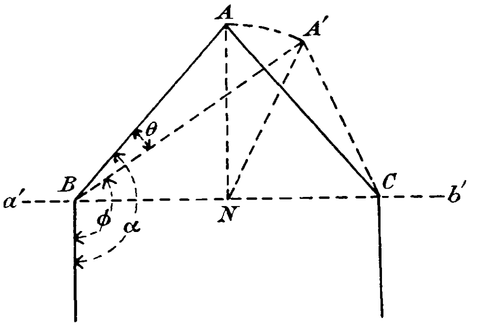


FIG. 2.



A mechanical model shows that when the quinonoid structure is distorted in the manner shown in Fig. 1, the valency bonds attaching substituted groups are deflected out of the plane of the ring by an equal amount but in an opposite sense to the movement of the CO groups. The moments of the disubstituted derivatives should, therefore, be greater or less (according to the direction of the moment of the substituted group) than that of *p*-benzoquinone. Hence, if the observed electrical moment of the quinones is due to this flexibility, the moment of the 2 : 5-dichloro-derivative should be less than that of quinone and equal to 2 sin θ ($\mu_{CO} - \mu_{Cl}$). θ being taken to be 8°, the moment of the CO link 2·5, and that of the C—Cl link 1·5, the moment of the derivative should be 0·26 D. This decrease is well outside experimental error and the equality of the moments of *p*-benzoquinone and its derivatives is a serious objection to the above flexibility hypothesis.

The four cyclic carbon atoms in 2 : 2 : 4 : 4-tetramethyl*cyclo*butane-1 : 3-dione are already strained by 19°28′ and so any considerable further straining of these bonds by thermal agitation is impossible, yet the difference between the total and the electron polarisation in benzene solution is 10·8 c.c., almost the same as that for *p*-benzoquinone and its derivatives. Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann (J., 1935, 1751) find for the two solutions they measured total polarisations of 42·9 and 45·9 c.c. A 10% addition to the electron polarisation, to allow for atom polarisation, gives a value of 41·3 c.c. From these figures they conclude that the moment is undetectably small. This conclusion is doubtful, as their solutions are rather dilute (0·00417 M and 0·00429 M) for accurate measurement of a substance with such a low polarisation. The $_{A+O}P_2$ value now reported is no less than 28·6% of the electron polarisation. The tetramethyl derivative was used rather than *cyclo*butanedione itself because with the latter there is enolisation (Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann, *loc. cit.*). Two samples of the tetramethyl derivative, prepared by different methods, were measured, the results being almost identical.

Further evidence against a slowly vibrating quinone molecule is obtained from a calculation of the vibration period. $\bar{P}$, the electrical polarisation due to vibration, is related to the moment, μ, of the vibrating group by the equation

$$\bar{P} = 4\pi N\mu^2/9V_0$$

(preceding paper), where V_0 is the bending force constant. In the case of *p*-benzoquinone $\bar{P}$ is approximately 9 c.c., $\mu = 2\cdot5 \times 10^{-18}$ e.s.u., and hence $V_0 = 5\cdot876 \times 10^{-13}$ erg/radian^2/molecule or 2·596 cals./degree^2/g.-mol. The period of the oscillation can be calculated from this force constant and if it is assumed that the motion is simple harmonic and of the type indicated in Fig. 1 a value of $5\cdot91 \times 10^{-13}$ sec. is obtained. The time of relaxation of medium-sized molecules is of the order of 10^{-11} to 10^{-12} sec. (Debye, *Trans. Faraday Soc.*, 1934, **30**, 679), so this type of oscillation leads to far too short a period to make any contribution to the orientation polarisation. The measurement of the refractive index of a benzene solution of *p*-benzoquinone in the far infra-red indicates a value of 9 to 16 c.c. for the excess of P_2 over ${}_EP_2$ at this frequency. This difference, however, can only be interpreted as atom polarisation if it can be shown that the molecule has no permanent dipole moment and that there is no solvent-solute interaction, which has not been done. Although the period of the oscillator postulated above is far too short for orientation polarisation to arise from bending, it in no way excludes the possibility of atom polarisation. If the mode of vibration studied is the correct one, it should lead to an absorption band with a maximum at a field-period of $5\cdot91 \times 10^{-13}$ sec., but the observed absorption band in the infra-red is at 120 cm.$^{-1}$ (p. 1266), *i.e.*, a period of $2\cdot8 \times 10^{-13}$ sec.

With the large strain which is already present in the four-membered ring the introduction of further strain by bending would require a large amount of energy. On the assumption, however, that it is possible and that the axis of vibration is that joining the two methylated carbon atoms, the force constant V_0, calculated from the polarisation, 10·8 c.c., is $4\cdot897 \times 10^{-13}$ erg/radian^2/molecule. This, for simple harmonic motion, gives a period of $5\cdot85 \times 10^{-13}$ sec., which again is much shorter than the normal time of relaxation.

The observed facts may be interpreted as follows. The equality of the moments of *p*-benzoquinone, its disubstituted derivatives, and 2 : 2 : 4 : 4-tetramethyl*cyclo*butane-1 : 3-dione practically rules out the possibility of the anomalous polarisation being due to bending in this particular mode. The calculated period of the oscillation is smaller than the time of relaxation and so eliminates the possibility of orientation polarisation arising from thermal vibrations. If the anomaly is due to atom polarisation, it cannot arise from vibrations of the type postulated, since the absorption band in the infra-red is at 120 cm.$^{-1}$. Two possible explanations remain : (1) The atom polarisation of compounds containing two carbonyl groups is abnormally large, but the vibrations causing this must be of a different type from those dealt with above. (2) With such compounds there is a general solvent effect, one applicable to all solvents. The measurement of the polarisations of the substances in the vapour state is the only means of enabling a decision between the two explanations to be made and such experiments are dealt with in the following paper. The conclusion that the molecule does not bend as the classical structure would lead one to expect demonstrates the inadequacy of this formulation. The considerable degree of rigidity of the ring is attributed to resonance.

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