Semi-empirical MNDO SCF-MO Study of Radicals derived from γ-Radiolysis of Tertiary Phosphines and Trialkylphosphites

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Calculations have been made, using the MNDO-UHF approximation, of the molecular and electronic structures of a range of phosphorus- and carbon-centred radicals formed in the γ-radiolysis of tertiary phosphines and of trialkylphosphites. The radical cations R_3P^+ are all calculated to have C_{3v} symmetry (for R = Me, Et, Pr^n, Bu^n): as the length of the alkyl chain increases, the phosphorus approaches more closely to planarity. In the radical cations $(RO)_3P^+$ (R = H, Me, Et), the geometry at phosphorus is close to tetrahedral: two conformers, of C_3 and C_s symmetry, were found for $(MeO)_3P^+$. Dinuclear cation radicals $(R_3P)_2^+$ and $[(RO)_3P]_2^+$ were found to be σ* radicals, having the SOMO strongly confined in the P–P bonds. $(H_3P)_2^+$ and $(Me_3P)_2^+$ are calculated to have D_{3d} symmetry: for $(Et_3P)_2^+$, $[(HO)_3P]_2^+$, and $[(MeO)_3P]_2^+$ two diastereoisomeric conformers, having D_3 and S_6 symmetry, were found.

There has been considerable interest in recent years[1–16] in the formation of phosphorus-centred and carbon-centred radicals, both neutral and charged, from tertiary phosphines R_3P and from trialkyl phosphites $(RO)_3P$. Amongst the features of interest concerning such radicals are: the structures of the cations R_3P^+ and $(RO)_3P^+$ formed by electron loss, and particularly the sum of bond angles at phosphorus;[2.6.9.13.16] the conformations of $(RO)_3P^+$;[16] the formation of dimeric ions $(R_3P)_2^+$ and $[(RO)_3P]_2^+$;[5.6.10.14–16] the possible phosphoranyl structures of the radicals formed by addition of either electrons or alkyl or alkoxy radicals, to R_3P or $(RO)_3P$;[3.6–8.10.14] and the structures and conformations of carbon-centred radicals derived from R_3P or $(RO)_3P$.[1.4.6.10] In the present paper we report semi-empirical SCF calculations, in the MNDO approximation, which are relevant to a number of these questions.

Calculations

All calculations were made using the MNDO method[17–19] employing *s* and *p* orbitals only, and with the published parameterisation for phosphorus.[20] UHF wavefunctions were employed for all open-shell species, and all geometric variables were simultaneously optimised, without the imposition of any constraints, unless specifically stated to the contrary.

Results and Discussion

Exposure of trialkyl phosphines and trialkyl phosphites to γ-irradiation in glasses or in frozen solutions can give rise to a wide range of chemical processes, these include: (*i*) simple electron loss [equation (1)]; (*ii*) electron loss with bond formation [equation (2)]; (*iii*) hydrogen-atom loss to give carbon-centred radicals [equations (3*a* and *b*)]; (*iv*) addition of electrons, hydrogen atoms, or alkyl or alkoxyl radicals (derived either from the substrate or from the matrix material) to form phosphoranyl radicals [equations (4*a*—*c*)], (R,R′ = alkyl or alkoxy). It is convenient to discuss the structures of the radicals arising from process (1)—(4) separately, in turn.

$$R_3P \xrightarrow{\gamma} e^- + R_3P^+ \qquad (1)$$

$$2R_3P \xrightarrow{\gamma} e^- + [R_3P\overset{\cdot}{\underset{-}{}}PR_3]^+ \qquad (2)$$

$$R_2PCH_2R' \xrightarrow{\gamma} H^{\cdot} + R_2P\dot{C}HR \qquad (3a)$$

$$R_2POCH_2R' \longrightarrow H^{\cdot} + R_2PO\dot{C}HR' \qquad (3b)$$

$$R_3P + e^- \longrightarrow R_3P^- \qquad (4a)$$

$$R_3P + H^{\cdot} \longrightarrow R_3PH^{\cdot} \qquad (4b)$$

$$R_3P + R' \longrightarrow R_3PR' \qquad (4c)$$

Structures of Radical Cations R_3P^+ *and* $(RO)_3P^+$.—Table 1 records optimised values of ΔH_f°, $X\hat{P}X$, and $\rho[P(3s)]$ for a range of R_3P^+ and $(RO)_3P^+$ cation radicals, together with values of the observed isotropic $A(^{31}P)$ values and the $X\hat{P}X$ angles derived from the observed hybridisation ratios.[2.9.16]

For the trialkylphosphine cations, there is a modest but steady increase in the angle $C\hat{P}C$ as the unbranched alkyl chain increases in length. Since all these cations adopt conformations of C_{3v} symmetry (C_3 conformations having the alkyl chains in approximately the same plane as the central PC_3 fragment are typically 10—15 kJ mol^{-1} higher in energy), any steric effect upon the central atom geometry is minimal. Rather the variation in $C\hat{P}C$ is the consequence[21] of the increasing electron-donor ability of the longer alkyl chains, well illustrated by the residual charges at phosphorus: q(P) in Me_3P^+, +0.185; Et_3P^+, +0.173; Pr_3P^+, +0.168; Bu_3P^+, +0.164.

This behaviour contrasts with that of $Me_3C^{\cdot}$ where a strong coupling of the alkyl group rotation to the skeletal bending has been found[22] in an *ab initio* study.

Table 1 contains a comparison of the angles $X\hat{P}X$ derived both from the MNDO calculations and from the e.s.r. spectra.[2.16] The calculation of the hybridisation ratio λ requires precise values of both $A_{\parallel}$ and $A_{\perp}$ and it is unfortunate that the complete series of Table 1 has not been studied in a single matrix medium. The values of A are somewhat sensitive to the matrix as exemplified by PBu_3^+: in sulphuric acid matrices the $A_{\parallel}$ and $A_{\perp}$ values are[2] 556 and 262 G, respectively, leading to a calculated angle $C\hat{P}C$ of 115.6°, while in $FCCl_3$ the A values are 529 and 247 G, giving $C\hat{P}C$ of 115.8°. Hence the angles calculated from λ are not strictly comparable for different matrices: this matrix effect probably accounts for the non-monotonic variation of both the e.s.r. value of $C\hat{P}C$ (as distinct from the monotonic variation of the MNDO values) and the isotropic A value. In addition, of course, the accurate calculation of geometry from λ requires the assumption of strict orbital following.

We note here that the isoelectronic series of radicals $AlR_3^{\cdot -}$,[2.23.24] $SiR_3^{\cdot}$,[2.25] and PR_3^+ all have pyramidal geometry[26] at the central atom, whereas the first-row analogues BR_3^-,[27.28] $CR_3^{\cdot}$,[22.29.30] and NR_3^+[31–33] all have planar

Table 1. Calculated and observed parameters of R_3P^+ and $(RO)_3P^+$

Radical	ΔH_f°/kJ mol^{-1}	$X\hat{P}X$/°[a]	$X\hat{P}X$/°[b]	$A(^{31}P)$/G[c]	$\rho[P(3s)]$
PH_3^+	1 029.9	113.1	113.9[d]	517[d]	0.140
PMe_3^+	664.0	118.1	115.7	385	0.077
PEt_3^+	572.0	118.4	115.5[d]	384[d]	0.074
PPr_3^+	505.1	118.6	*e*	*e*	0.074
PBu_3^+	443.5	118.9	115.8	341	0.074
$P(OH)_3^+$	40.7[f]	108.1	109.5	795[g]	0.192
$P(OMe)_3^+$	44.2[f]	107.0	110.1[h]	870[h]	0.160
	62.7[i]	*j*	108.7[h]	776[h]	0.131
$P(OEt)_3^+$	−36.9[f]	107.3	109.5[k]	767[k]	0.161
	−19.1[i]	*l*			0.131

[a] Angle calculated by MNDO. [b] Angle calculated from observed hybridisation ration λ, in $FCCl_3$ or CCl_4. [c] Isotropic value; G = 10^{-4} T; values from ref. 16, unless otherwise stated, for samples in $FCCl_3$ or CCl_4 matrices. [d] Ref. 2; samples in sulphuric acid matrices. [e] Not recorded. [f] C_3 symmetry, free optimisation. [g] Ref. 9. [h] Two conformers observed (ref. 16); see text. [i] C_s symmetry, constrained optimisation. [j] $O\hat{P}O$ angles are 102.3° (× 2), 109.3° (× 1). [k] Conformer not definitively identified; see text. [l] $O\hat{P}O$ angles are 102.3° (× 2), 109.5° (× 1).

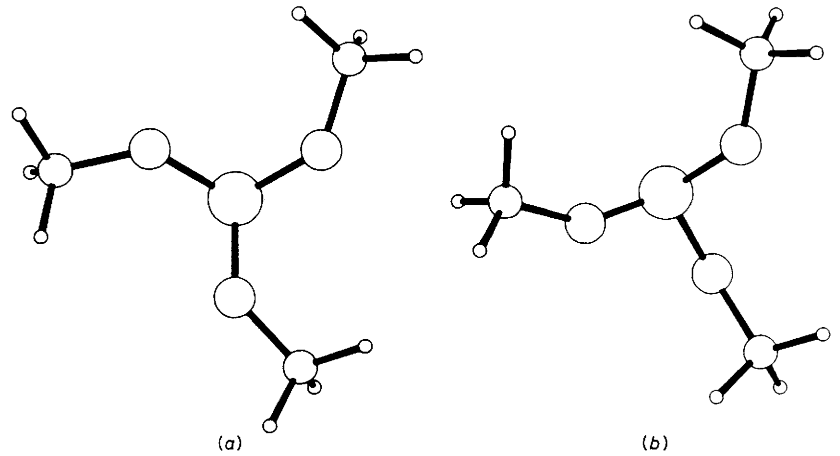
(a) (b)

Figure 1. (*a*) The C_3 conformer of $(MeO)_3P^+$, viewed down the symmetry axis; (*b*) the C_s conformer of $(MeO)_3P^+$, viewed down the symmetry plane

skeletons consistent[21] with their higher central atom electronegativity.

In contrast to the alkyl phosphine cations are those derived from trialkyl phosphites, which have almost tetrahedral geometry at phosphorus whether calculated by MNDO or derived[16] from the e.s.r. parameters: similarly the cation $P(OH)_3^+$, produced[9] upon γ-irradiation of phosphoric acid in a frozen sulphuric acid matrix, is close to tetrahedral at phosphorus. This is almost certainly a consequence[21] of the much higher electronegativity of the oxygen ligands as compared with the carbon ligands of the trialkylphosphine cations: accordingly the calculated charges at phosphorus, q(P), in the C_3 conformers of $P(OH)_3^+$, $P(OMe)_3^+$, and $P(OEt)_3^+$ are +1.220, +1.217, and +1.208, respectively, compared with the values of less than +0.2 for the trialkylphosphine cations, noted above. Consistent with the much steeper pyramidality at phosphorus in $P(OR)_3^+$, both the observed[16] A values and the calculated $\rho[P(3s)]$ values are substantially larger in $P(OR)_3^+$ than in PR_3^+. In both PR_3^+ and $P(OR)_3^+$ there is a satisfactory agreement between the MNDO geometries and those derived from the e.s.r. data.

In attempting to establish a scale factor between the isotropic $A(^{31}P)$ and $\rho[P(3s)]$ appropriate to the MNDO parameterisation it must be borne in mind that ρ is derived from a calculation on an isolated radical whereas A is the value measured for a radical usually in a solid matrix, and that A varies somewhat[2,16] with matrix material. Subject to these cautions, reasonable correlation of A and ρ is obtained for the radicals in Table 1, yielding a scale factor A/ρ of 4 600 ± 400.

When $(MeO)_3P$ is γ-irradiated in frozen halogenocarbon matrices, two distinct species are formed[16] whose relative proportions change smoothly across a series of mixed CCl_4–$CFCl_3$ matrices, and it was suggested that these species are two distinct conformers of $(MeO)_3P^+$: the ratio of $A_{iso}(P)$ for the two conformers is 1.12. Optimisation of the structure of $(MeO)_3P^+$ without constraint yields a structure of C_3 symmetry [Figure 1(*a*) and Table 1]: imposition of C_s symmetry gives a structure [Figure 1(*b*)] whose energy is some 18.5 kJ mol^{-1} higher than the C_3 conformer, and whose $\rho[P(3s)]$ value is rather smaller; the ratio of $\rho[P(3s)]$ for these two conformers is 1.22. In the C_3 conformer the SOMO has A_1 symmetry, with oxygen 2*s* spin-density, $\rho[O(2s)]$, of -0.65×10^{-3}: in the C_s conformer, the SOMO, of A' symmetry, has $\rho[O(2s)]$ of -4.04×10^{-3} for the unique oxygen and -1.15×10^{-3} for the symmetry-related pair of oxygens. In these particulars the calculations are in agreement with the experimental observation that the conformer of lower $A_{iso}(P)$ has a greater spin-delocalisation on to oxygen: we therefore conclude that the C_3 and C_s conformers are reasonable representations of the structures of $(MeO)_3P^+$ in CCl_4 and $CFCl_3$ matrices, respectively, although we have no explanation of why one conformer is specifically preferred in each matrix.

It is a remarkable observation that, regardless of whether the matrix material is CCl_4 or $CFCl_3$, $(EtO)_3P$ unlike its methyl

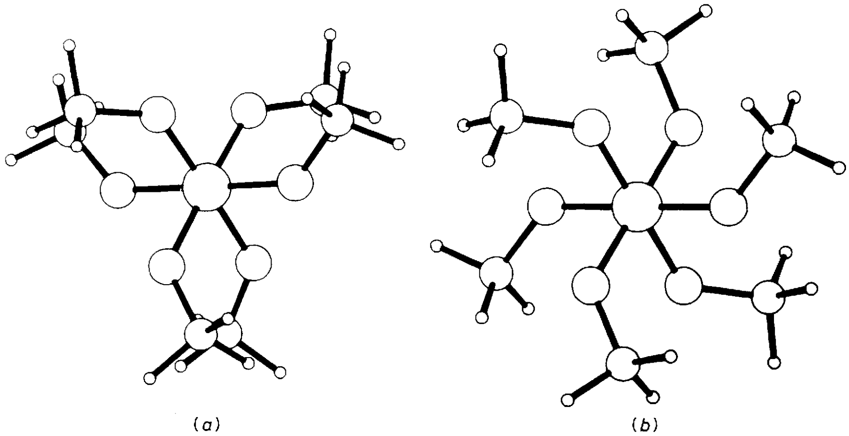

Figure 2. (*a*) The D_3 conformer of $[(MeO)_3P]_2^+$; (*b*) the S_6 conformer of $[(MeO)_3P]_2^+$; in each case viewed along the P–P direction

Table 2. Calculated and observed parameters for $(R_3P)_2^+$ and $[(RO)_3P]_2^+$

Dimer	ΔH_f°/kJ mol^{-1}	d(P–P)/Å	$X\hat{P}X/^{\circ a}$	$X\hat{P}X/^{\circ b}$	$A(^{31}P)/G^c$	$\rho[P(3s)]$
$P_2H_6^+$	+792.6	2.080	104.9	*d*	*d*	0.174
$P_2Me_6^+$	+286.1	2.174	108.1	110.3	503	0.137
$P_2Et_6^+$	+218.9^e	2.254^e	107.8^e	111.4	460	0.130^e
	+214.4^f	2.252^f	105.9^f			0.132^f
$P_2(OH)_6^+$	−906.2^e	2.327^e	105.7^e	*d*	*d*	0.171^e
	−908.3^f	2.324^f	105.7^f			0.170^f
$P_2(OMe)_6^+$	−827.8^e	2.356^e	106.6^e	107.3	670	0.163^e
	−830.8^f	2.353^f	106.5^f			0.161^f
$P_2(OEt)_6^+$	*g*	*g*	*g*	106.6	665	*g*

[a] Angle calculated by MNDO. [b] Angle calculated from observed λ. [c] Isotropic values, ref. 16. [d] Not reported. [e] D_3 conformer. [f] S_6 conformer. [g] Not studied by MNDO calculation.

analogue gives only a single conformer. The data of Table 1 for two conformers of $(EtO)_3P^+$, having C_3 and C_s symmetry, respectively, suggest that the conformer actually observed is the less stable C_s form.

Structures of Dimer Cations $(R_3P)_2^+$ *and* $[(RO)_3P]_2^+$.—Dimer cations, of general type $(L_3P)_2^+$, have been observed for L = Me,[15,16] Et,[5,16] Bu^n,[5] Ph,[5] MeO,[6,10,14,16] and EtO,[16] although not apparently for L = H. These dimeric species have all been regarded[15,16] as σ* radicals in which the SOMO is an antibonding orbital concentrated primarily in the P–P bond: similar σ* species $(L_nM)_2^+$ have been observed for M = As,[5] S,[34] Se,[35] and Cl, Br, and I,[36] and L = alkyl. The present MNDO calculations show that the species $(L_3P)_2^+$ having L = H, Me, Et, and MeO are all σ* radicals having symmetric molecular and electronic structures in which the two L_3P 'halves' of the cation are equivalent: in each case the immediate X_3PPX_3 core of the radical has an ethane-type configuration of exact D_{3d} symmetry, with a σ* SOMO of A_{2u} symmetry in the local D_{3d} microsymmetry. The overall molecular symmetry of both $P_2H_6^+$ and $P_2Me_6^+$ (discounting the free rotation of the methyl groups) is D_{3d}, but for $P_2Et_6^+$, $P_2(OH)_6^+$, and $P_2(OMe)_6^+$, two conformers were found, having D_3 and S_6 symmetry, respectively (Figure 2). It is of interest that each of the conformers is formed from a combination of two mononuclear fragments, each of which has C_3 symmetry, and hence is chiral. Combination of two fragments, each of the same chirality, gives a dimer of D_3 symmetry, regardless of the dihedral angle relating the two 'halves'. However, the combination of two fragments of opposite chirality gives a dimer whose symmetry is S_6 in the fully staggered conformation [Figure 2(*b*)], C_{3h} in the fully eclipsed conformation, and only C_3 otherwise. For each of $P_2Et_6^+$, $P_2(OH)_6^+$, and $P_2(OMe)_6^+$, the energies and the molecular and electronic structures of the diastereoisomeric D_3 and S_6 forms differed very little (Table 2).

Comparison of the data in Tables 1 and 2 reveals immediately that for PH_3^+, and for the alkyl species PR_3^+, there is a significant reduction in the angle $X\hat{P}X$ upon dimer formation, associated with an increase in both $A(^{31}P)$ and $\rho[P(3s)]$: on the other hand, for alkoxy species $P(OR)_3^+$, the changes in $X\hat{P}X$, and in A and ρ, are much more modest, since in $P(OR)_3^+$ the bond angles at phosphorus are close to the tetrahedral value even in the monomers. As with the monomeric species, the bond angles calculated for $(R_3P)_2^+$ and $[(RO)_3P]_2^+$ by MNDO are in satisfactory agreement overall with those derived from the e.s.r. data.

In terms of the variation of the angle $X\hat{P}X$ between monomer and dimer, σ* dimer formation from $(RO)_3P^+$ resembles σ dimer formation from $R_3Si^{\bullet}$ rather than σ* dimer formation from R_3P^+ (Tables 1 and 2, and reference 37). Formation of $(Me_3Si)_2^+$ from Me_3Si^+ and $Me_3Si^{\bullet}$ occasioned a change in $C\hat{Si}C$ in the radical from 113.5°, only to 114.8°, while formation of $(Me_3P)_2^+$ from Me_3P^+ is associated with a much bigger change. Associated with these dimerisation processes are changes in $A(^1H)$, observed[15] to be small for the trimethylsilicon system, but much larger for the trimethylphosphine system; we have argued,[37] however, from the results of MNDO calculations that the changes in $A(^1H)$ are dominated by the character, σ or σ*, of the SOMO.

In the present context, the important parameters seem to be values of $A(M)$ and $\rho[M(3s)]$ (Table 3), whose behaviour depend both on geometry and on the character of the SOMO.

Table 3. Values of A(M) and ρ[M(3s)] for representative σ and σ^* dimer cations, and their monomers

Monomer	$A(M)$/G[a]	$\rho[M(3s)]$	Dimer	$A(M)$/G[a]	$\rho[M(3s)]$
$Me_3Si^{\cdot}$	191[b]	0.205	$Me_6Si_2{}^+$	c	0.005
Me_3P^+	385	0.077	$Me_6P_2{}^+$	503	0.137
$(MeO)_3P^+$	870 776 [d]	0.160	$(MeO)_6P_2{}^+$	670	0.163

[a] M = ^{29}Si, ^{31}P; G = 10^{-4} T; values from ref. 16 unless otherwise stated. [b] Ref. 38. [c] Not observed (refs. 39 and 40). [d] Two conformers (ref. 16).

For the σ^* radicals, A and ρ are closely dependent on the geometry at phosphorus. For the silicon σ system, a very small change in geometry at silicon occurs upon dimer formation, while it causes only a modest variation in $A(^1H)$[38–40] and in $\rho[H(1s)]$,[37] is calculated to cause a major decrease in [Si(3s)]. The coupling $A(^{29}Si)$ was not observed[39,40] in $Me_6Si_2{}^+$, whereas it was resolved[38] for $Me_3Si^{\cdot}$: the present calculations suggest that $A(^{29}Si)$ in $Me_6Si_2{}^+$ will only be *ca.* 5 G.

Structures of Carbon-centred Radicals.—Loss of hydrogen atoms upon γ-irradiation can occur from carbon atoms either α to phosphorus, as in $P(CH_2OH)_3$[1] or Et_3P and Et_3PH^+,[4] or β to phosphorus, as in $(MeO)_3P$.[6,10] We have made calculations on the conformations of three such carbon-centred radicals, $(MeO)_2PO\dot{C}H_2$,[6,10] $Et_2P\dot{C}HMe$,[4] and $Et_2\overset{+}{P}(H)\dot{C}HMe$.[4]

The radical $(MeO)_2PO\dot{C}H_2$ is formed, along with many others, by γ-irradiation of $(MeO)_3P$, either as a glass[10] or as a frozen solution in methanol[6]: it is characterised by $A(^1H)$ of 21—22 G due to the CH_2 group, but no hyperfine coupling to phosphorus was observed. In the calculated structure there is a planar $POCH_2$ fragment in which the SOMO is a π^* orbital concentrated on oxygen and carbon; $\rho[P(3s)]$ is calculated to be negligibly small (9×10^{-6}) consistent with the lack of resolution of $A(^{31}P)$.[6,10] Rotation of the CH_2 group through 90° about the C–O bond caused an increase in $\Delta H_f^{\ominus}$ of only 3.4 kJ mol^{-1}, with no significant change in the distribution of spin density.

This very low barrier to rotation of the CH_2 group is ascribed to the presence of two formally non-bonding orbitals, mutually perpendicular, on the unique oxygen atom; delocalisation of the electron hole of the SOMO into either of these orbitals is equally possible.

In $Et_2P\dot{C}HMe$, where the radical centre is again planar having the SOMO concentrated in a $p\pi$ orbital of carbon, there is a single non-bonding orbital on the adjacent phosphorus. The electron hole is delocalised into this orbital, giving a minimum-energy conformation having a dihedral angle of zero between the SOMO and the lone-pair orbital of phosphorus. The barrier to rotation here is calculated as 7.1 kJ mol^{-1}.

The protonated analogue $Et_2\overset{+}{P}(H)\dot{C}HMe$, having a similar SOMO to $Et_2P\dot{C}HMe$, has no lone-pair orbitals at all into which the electron hole may be delocalised. The electron hole is not in fact readily delocalised into the P–H bond, but rather into the less deeply bound P–C bonds of the two intact ethyl groups, giving a minimum-energy conformation in which the dihedral angle between the SOMO and the P–H bond is 90°. The rotational barrier about the unique P–C bond is calculated as 19.4 kJ mol^{-1}, much higher than in $(MeO)_2PO\dot{C}H_2$ and $Et_2P\dot{C}HMe$ where there is at least one lone-pair orbital α to the radical centre.

Phosphoranyl Radicals.—No satisfactory optimisations were achieved for $(MeO)_3P^-$, $(MeO)_3PH$, $(MeO)_3PMe$ or $(MeO)_4P$: the structures obtained for the first three of these radicals had C_3 symmetry, with angles at phosphorus close to tetrahedral, while that for $(MeO)_4P$ had S_4 symmetry. In all cases the SOMO was calculated to be of σ^*(P–X) type with X = O in $(MeO)_3P^-$ and $(MeO)_4P$, X = C in $(MeO)_3PMe$, and X = H in $(MeO)_3PH$; no phosphoranyl structures were found for any radical. We conclude that a basis of s and p orbitals only is inadequate for the description of these systems, which is in any event complicated by the possibility of pseudorotation, and that d orbitals must be included in the description.

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