

**8. Solvent-Shared Radical Ion Pairs [Pyrene^{•-}Na⁺O(C₂H₅)₂]_∞:
ESR Evidence for Two Different Aggregates in Solution,
Room Temperature Crystallization, and Structural Proof of Another
Polymorphic Modification¹⁾**

by **Christian Näther** and **Hans Bock***

Institute of Inorganic Chemistry, Johann Wolfgang Goethe University Frankfurt, Marie-Curie-Str. 11,
D-60439 Frankfurt

and **Rodney F. C. Claridge**

Chemistry Department, University of Canterbury, Christchurch, New Zealand

Dedicated to *Kurt Dehnicke* on the occasion of his 65th birthday

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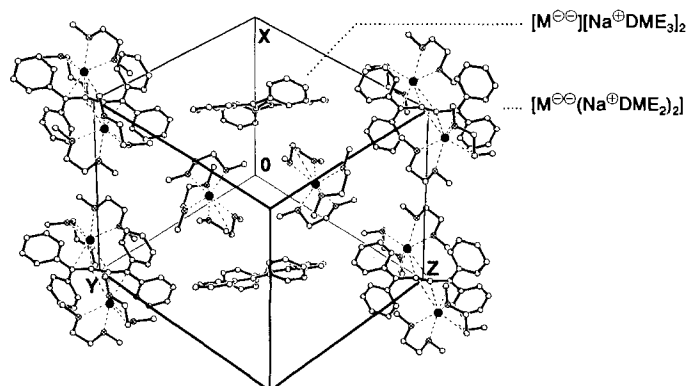
The reduction of pyrene with sodium in aprotic diethyl ether allows to crystallize the extremely air-sensitive radical ion pair pyrene-sodium-diethylether. The single-crystal structure determination at 130 K shows that each sodium counter cation, solvated by one diethyl-ether molecule, is η^3 - and η^6 -coordinated to one of the short-axis six-membered rings of two pyrene radical anions. The resulting dibenzene-sodium sandwiches form a string, in which the hydrocarbon planes are canted to each other by 62°. In the pyrene radical-anion skeleton, no distortion due to its negative charge can be detected relative to that of the neutral molecule. From the temperature-dependent signal multiplets of preceding ESR investigations, the solvent-separated pyrene radical anion as well as two different contact radical-ion pairs had been identified and their structures in solution approximated by potential-energy estimates. Referring to the recently discovered long-axis Na⁺ contact ion pair polymorph, crystallized at lower temperatures, the structure reported here represents the second and probably thermodynamically more stable one. Both the ESR and the structural results provide some insight into the multidimensional networks of equilibria in aprotic solution, which are activated by alkali-metal reduction of unsaturated organic compounds.

Introduction. – Systematic structural studies of alkali metalorganic compounds [1–3] have considerably improved a rationalization of both their physical properties and their reactivity. More essential, however, might be the experience and knowledge gathered concerning cation-solvation phenomena [2] [4–6], which govern a multitude of reactions including those of bio- or geochemical importance. Of special value is all structural information, which suggests in addition whether the cation coordination in the molecular crystal should closely resemble that of the solvate ligand complex in solution [2] [4–6]. This provides an advantageous starting point for investigations aiming at an insight into the multidimensional network of electron transfer and contact-ion formation, as well as aggregation, disproportionation, and solvation equilibria activated by a redox reaction. In these rather rare cases, the detailed data from the crystal-structure analysis can be correlated with the results from methods such as NMR, ESR, or UV/VIS spectroscopy.

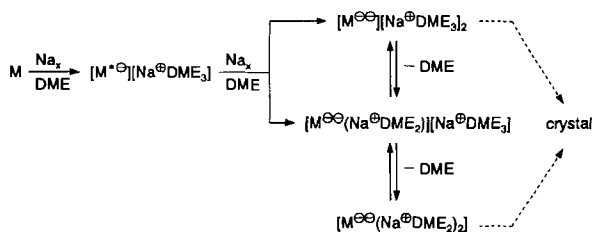
¹⁾ Part 85 of Interactions in Molecular Crystals; Part 84: [1].

From a dimethoxyethane solution of 1,1,4,4-tetraphenylbutadiene-disodium, for instance, both the solvent-shared and solvent-separated ion multiples, $[M^{\ominus\ominus}(Na^{\oplus}DME_2)_2]$ and $[M^{\ominus\ominus}][Na^{\oplus}DME_3]_2$, crystallize simultaneously in a 1:1 stoichiometric ratio [6] (Scheme 1). In addition to all the detailed data from the low-temperature single-crystal

Scheme 1



Scheme 2

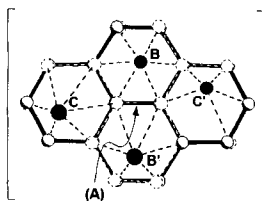


structure analysis, experimental evidence is provided for a solvation segment (Scheme 2) of the multidimensional equilibria network, within which the 'simple' two-electron reduction of tetraphenylbutadiene by Na to its dianion is accomplished.

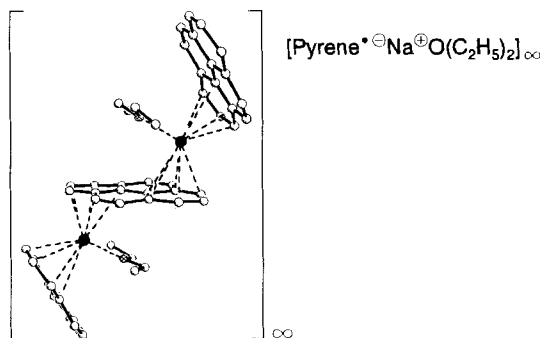
In 1976, a preceding ESR study of the pyrene radical anion in various etheral solvents, generated by reduction with various alkali metals, and varying the measurement temperature, yielded a wealth of thermodynamic data [7]. For the Li/Et₂O system, three different species could be identified by their temperature-dependent hyperfine splitting multiplets: the 'free' pyrene radical anion as well as rapidly interconverting 'tight' and 'loose' contact ion pairs, of which the 'tight' one proved to be more stable in solution at higher temperature. For the Na/Et₂O system similar observations were made, but the existence of two different ion pairs could not be established with certainty due to the small size of the Na coupling. Interpretation of the ESR data based on a crude potential-energy model suggested the following preferred counter-cation locations above the molecular plane of

the pyrene radical anion [7] [8]: for the 'tight' ion pair a site above one of the 'short-axis' pyrene six-membered rings (*Scheme 3, B or B'*) and for the 'loose' ion pair above one of the 'long-axis' carbon hexagons (*Scheme 3, C or C'*).

Scheme 3



Scheme 4



A position above the central C,C bond (*Scheme 3, A*) has been discarded for various reasons as being less likely [7] [8]. On the contrary, especially at small interionic distances the symmetry-equivalent positions *B* and *B'* are regarded to yield the most stable contact ion pairs.

Eight years later, a sodium radical-anion salt of pyrene could be crystallized from Et₂O solution at lower temperatures and structurally characterized (*Scheme 4*) [9]. The crystal-structure determination proved an infinite string of contact ion pairs, and that the Na[⊕] counter cation is located at a distance of 253 pm to the molecular plane of the pyrene radical anion alternating between the symmetry-equivalent positions above the 'long-axis' six-membered rings (*Scheme 3, C and C'*). The Na[⊕] cations each bridge two radical anions, and their coordination spheres are completed by one Et₂O. The infinite columns of the pyrene radical anions are arranged along the crystallographic *a*-axis, and the hydrocarbon planes are canted to each other by 60° [9].

Stimulated by the above ESR [7] [8] as well as by the structural results [9] (*Schemes 3 and 4*), the reduction of pyrene by Li and Na metal mirrors has been reinvestigated on a preparative scale in order to isolate other potential contact ion pairs from the aprotic Et₂O solutions. In both attempts, we succeeded in growing crystals: whereas those of pyrene-lithium-diethylether due to their extreme air-sensitivity up to now have resisted X-ray analysis, the structural details of pyrene-sodium-diethylether can already be reported.

Crystallization and Structure of Pyrene-Sodium-Diethylether. – The crystals have been obtained by slow removal of the solvent from the Et₂O solution at *ca.* 30° in a sealed-off two-bulb glass apparatus (*cf. Experimental*). Under these ‘higher-temperature’ conditions (*cf.* [9]), the solvent-shared radical contact ion pair crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent complexes in the asymmetric unit, each located around a center of inversion (*Fig. a*).

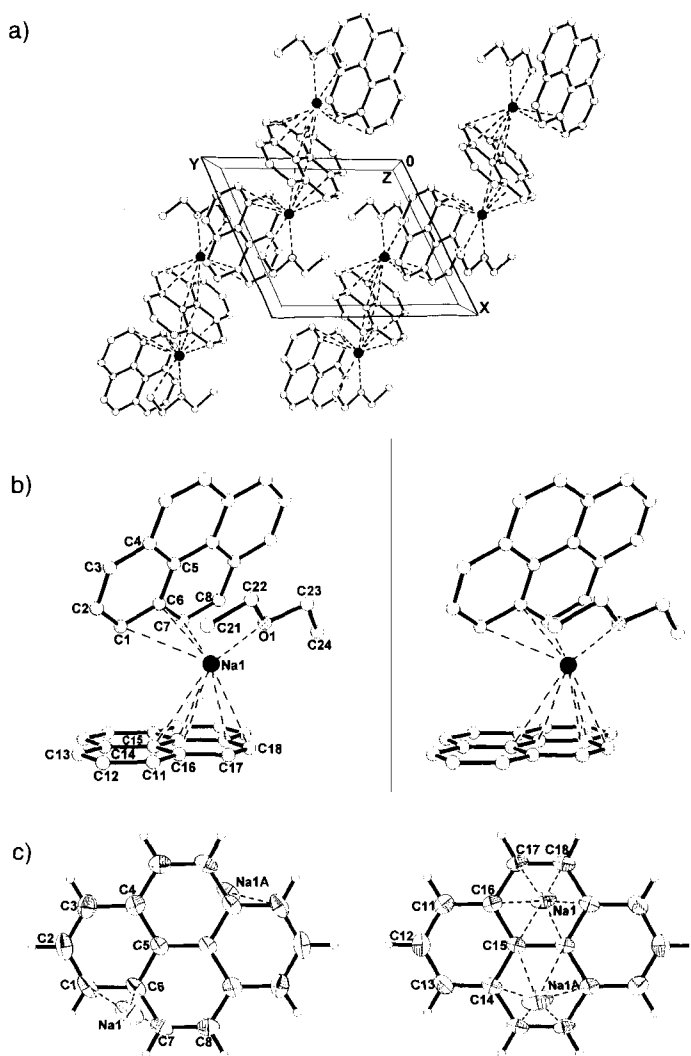


Figure. Single-crystal structure of the solvent-shared radical ion pair $[\text{pyrene}^{\ominus}\text{Na}^{\oplus}\text{O}(\text{C}_2\text{H}_5)_2]_{\infty}$. a) Segment of the infinite coordination strings including the unit cell (triclinic $P\bar{1}$, $Z = 2$) in z -direction, b) side view of two pyrene radical anions bridged by $\text{Na}^{\oplus}\text{O}(\text{C}_2\text{H}_5)_2$ (with numbering) and c) top view onto the molecular planes of the pyrene radical anions with differing coordination to the cation centers Na(1) and Na(1A) (50% thermal ellipsoids; structural data, see the Table).

The structures of the two crystallographically independent pyrene radical anions (*Fig.*, *b*, and *Table*) do not show any significant geometric distortions relative to the neutral pyrene molecule [10] [12], which indicates that the single negative charge is well-delocalized over the large planar π system. As concerns the planarity of the hydrocarbon skeleton, no individual C-centers deviate more than 1.8 (2) pm from an idealized least-squares plane. All these structural details are in accord with the general experience [1] [13] [14] that geometry distortions due to charge-perturbation are observed predominantly after two-electron reduction to hydrocarbon dianions, whereas structural changes due to one-electron transfer usually can only be detected in small π systems [1] [13] [14].

Each pyrene radical anion is connected to two Na^{\oplus} counter cations, one below and one above the molecular plane (*Fig.*, *c* and *d*). In the resulting contact ion pair polymer, the Na^{\oplus} counter cations accordingly exhibit two different coordination spheres (*Fig.*, *b*,

Table. Selected Structural Data for the Radical Ion Pair $[\text{Pyrene}^{\ominus}\text{Na}^{\oplus}\text{O}(\text{C}_2\text{H}_5)_2]_{\infty}$
(distances in pm, angles in $^{\circ}$; for numbering, see *Fig.*, *b* and *c*)

<i>Independent molecule I</i>			
C(1)–C(2)	137.7 (3)	C(1)–C(6)	142.0 (3)
C(2)–C(3)	138.2 (3)	C(3)–C(4)	141.8 (3)
C(4)–C(8A)	141.3 (3)	C(4)–C(5)	142.9 (3)
C(5)–C(5A)	142.8 (4)	C(5)–C(6)	143.5 (2)
C(6)–C(7)	141.4 (3)	C(7)–C(8)	137.2 (3)
C(8)–C(4A)	141.3 (3)		
C(2)–C(1)–C(6)	120.7 (2)	C(1)–C(2)–C(3)	121.8 (2)
C(2)–C(3)–C(4)	120.4 (2)	C(8A)–C(4)–C(3)	123.0 (2)
C(8A)–C(4)–C(5)	118.3 (2)	C(3)–C(4)–C(5)	118.7 (2)
C(5A)–C(5)–C(4)	120.3 (2)	C(5A)–C(5)–C(6)	119.6 (2)
C(4)–C(5)–C(6)	120.1 (2)	C(7)–C(6)–C(1)	123.2 (2)
C(7)–C(6)–C(5)	118.4 (2)	C(1)–C(6)–C(5)	118.3 (2)
C(8)–C(7)–C(6)	121.6 (2)	C(7)–C(8)–C(4A)	121.8 (2)
<i>Independent molecule II</i>			
C(11)–C(12)	138.6 (3)	C(11)–C(16)	142.6 (3)
C(12)–C(13)	138.4 (3)	C(13)–C(14)	142.7 (3)
C(14)–C(18A)	141.1 (3)	C(14)–C(15)	143.6 (3)
C(15)–C(16)	143.1 (2)	C(15)–C(15A)	143.7 (4)
C(16)–C(17)	141.3 (3)	C(17)–C(18)	137.6 (3)
C(18)–C(14A)	141.1 (3)		
C(12)–C(11)–C(16)	120.4 (2)	C(13)–C(12)–C(11)	122.1 (2)
C(12)–C(13)–C(14)	120.1 (2)	C(18A)–C(14)–C(13)	123.1 (2)
C(18A)–C(14)–C(15)	118.3 (2)	C(13)–C(14)–C(15)	118.6 (2)
C(16)–C(15)–C(14)	120.4 (2)	C(16)–C(15)–C(15A)	119.8 (2)
C(14)–C(15)–C(15A)	119.9 (2)	C(17)–C(16)–C(11)	123.0 (2)
C(17)–C(16)–C(15)	118.5 (2)	C(11)–C(16)–C(15)	118.5 (2)
C(18)–C(17)–C(16)	121.7 (2)	C(17)–C(18)–C(14A)	121.9 (2)
<i>Coordination distances</i>			
Na(1)–C(1)	296.2 (2)	Na(1)–C(6)	263.1 (2)
Na(1)–C(7)	276.7 (2)	Na(1)–C(14A)	283.8 (2)
Na(1)–C(15A)	297.0 (2)	Na(1)–C(15)	300.3 (2)
Na(1)–C(16)	290.7 (2)	Na(1)–C(17)	277.0 (2)
Na(1)–C(18)	273.0 (2)	Na(1)–O(1)	225.2 (2)

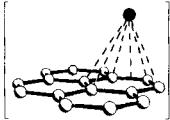
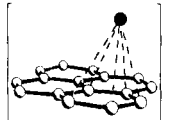
and Table). The strongest interaction of η^6 -type with one of the 'short-axis' six-membered rings of the naphthalene subunit in the pyrene radical anion (Scheme 3, B, and Fig., c), locates the Na^\oplus center 248 (2) pm above the C plane and leads to distances $\text{Na}^\oplus \cdots \text{C}^{\delta\ominus}$ between 273 and 300 pm with the shortest ones to centers C(17) and C(18) (Table: 273.0 (2) and 277.0 (2) pm). The η^3 -coordination to the other independent pyrene radical anion (Fig., c) exhibits distances $\text{Na}^\oplus \cdots \text{C}^{\delta\ominus}$ between 263 and 296 pm, including the shortest one of all to C(6) (Table: 263.1 (2) pm). The multihapto interactions of the bridging links $\text{Na}^\oplus\text{OEt}_2$ with two different pyrene radical anions are the underlying principle of the one-dimensional polymeric structure (Fig., a) in which the hydrocarbon planes are canted to each other by 61.53 (3) $^\circ$ (Fig., d).

Coordination Polymorphism. – The structure of the radical salt [pyrene $^\ominus\text{Na}^\oplus\text{O}(\text{C}_2\text{H}_5)_2$] $_\infty$ presented (Fig.) is one of the rather few examples for a solvent-shared contact ion pair of a π -hydrocarbon radical anion, the first one, to the best of our knowledge, being the other structure of pyrene-sodium-diethylether (Scheme 4) determined three years ago [9]. In general, an extensive delocalization of a single negative charge over a large π -system does not produce preferred cation docking sites [1] [5] [15–19]. Only, if relatively poor solvating solvents such as Et_2O [9] are used, or if electron-rich hetero centers such as N or O are present in the respective radical anion [20–22], crystallization of solvent-shared contact ion pairs seems to be feasible.

On comparison of the two structures of pyrene-sodium-diethylether reported (Scheme 3 [9] and Fig.), which can be classified as being an example of rare or even the first 'coordination polymorphs' [23–26], the first question concerns the thermodynamically more stable one. Therefore, we have determined the cell constants of our compound (Fig.) in addition at the temperature of the structure determination of the other modification [9] (Scheme 4), and have found a significant higher density (1.241 vs. 1.227 g cm^{-3}). According to an empirical rule, the polymorph with the higher density should be the more stable one [25] [26], although a few exceptions are known.

The two polymorphic modifications of pyrene-sodium-diethylether (Fig. and Scheme 4 [9]) can be best characterized by the different coordination of the Na^\oplus counter cations. In our radical-ion salt, the distance of the η^6 -coordinated Na^\oplus to the pyrene 'short-axis' six-membered ring is found to be 248 pm (Scheme 3, B), in the one of lower density [9] the slightly unsymmetrical coordination is to the pyrene 'long-axis' six-membered ring (Scheme 3, C), and the distance $\text{Na}^\oplus \cdots \text{C}(6)$ amounts to 253 pm, i.e., is ca. 5 pm longer. The shortest distance $\text{Na}^\oplus \cdots \text{C}^{\delta\ominus}$ determined in [9], 262 pm, however matches the one for our polymorph. A least-squares fit for both radical ion pairs projected onto the mean plane of the pyrene C skeleton (Scheme 3) clearly shows the different coordination in the two 'coordination polymorphs', including the slightly unsymmetrically located Na^\oplus interacting with ring C (Scheme 3) [9]. Both positions, symmetrical above ring B and recognizably off-center above ring C, correspond to the energy minima proposed to rationalize the ESR-spectroscopically detected 'tight' and 'loose' contact ion pairs [7] [8]. According to the reported potential-energy estimates [7] [8], the Na^\oplus position above one of the 'short-axis' naphthalene subunit rings (Scheme 3, B) should be energetically more favorable than above one of the 'long-axis' biphenyl subunit rings (Scheme 3, C). In addition, MNDO enthalpies of formation [5] $\Delta/\Delta H_f^\circ[\text{M}^\ominus\text{Na}^\oplus] - \Delta H_f^\circ[\text{M}^\ominus]$, have been calculated for the following fragment (Scheme 5) based each on their structural data (in kJ mol^{-1}):

Scheme 5

		
ΔH_f° [$M^{\ominus}Na^{\oplus}$]	+ 67	+ 241
ΔH_f° [M^{\ominus}]	145	+ 315
$\Delta\Delta H_f^\circ$ [$\text{kJ}\cdot\text{mol}^{-1}$]	-78	-74

Even this crude approximation for the interaction between the pyrene radical anion and the Na^{\oplus} counter cation in the two different coordination polymorphs (Fig. and Scheme 4) predicts our crystal with its higher density (*Experimental*) to contain the more stable contact ion pair. If so, the ‘tighter’ and, according to the temperature-dependent ESR measurements, thermodynamically advantageous ion aggregate in solution should exhibit a largely comparable structure.

Retrospective and Perspectives. – Potential surfaces for ensembles such as presented are known to be shallow [5] [27]; individual ion pairs can exhibit different structures [6] [28], and semiempirical estimates for fragments (Scheme 5) may be of questionable reliability. Nevertheless, the ESR data for the ‘tighter’ Na^{\oplus} contact ion pair in solution, the ‘higher-temperature’ crystallization conditions, and, above all, the crystal structure presented and its realization to potentially be the more stable coordination polymorph fit together rather well.

In summary, investigations combining ESR spectroscopy in solution and structure analysis of crystallized coordination polymorphs allow to better understand the complex equilibria networks of electron-transfer reactions [2] and, therefore, should be pursued with intensity.

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Experimental. – *Crystallization of $[\text{Pyrene}^{\ominus}\text{Na}^{\oplus}\text{O}(\text{C}_2\text{H}_5)]_{\infty}$.* Pyrene (5 mg) is dissolved in Et_2O (3 ml), and the soln. brought into contact with a Na mirror generated at 10^{-5} mbar pressure in a sealed glass apparatus consisting of two interconnected 5-ml bulbs. The reduction at the Na mirror produces a deep red soln., from which small red crystals grow in *ca.* 10 days at r.t., if the other bulb of the glass apparatus is kept in water.

Crystal-Structure Determination. [$\text{Pyrene}^{\ominus}\text{Na}^{\oplus}\text{O}(\text{C}_2\text{H}_5)_2$] $_{\text{cr}}$, red plates, $\text{C}_{20}\text{H}_{20}\text{ONa}\cdot\text{C}_4\text{H}_{10}\text{O}$ (mol.-wt. = 299.35 g mol^{-1} , $a = 878.9$ (1), $b = 1008.4$ (1), $c = 1049.5$ (1) pm, $\alpha = 102.404$ (8), $\beta = 106.097$ (6), $\gamma = 109.676$ (7) $^\circ$, $V = 791.2\cdot 10^6$, pm^3 ($T = 130$ K), $\rho_{\text{ber}} = 1.257$ g cm^{-3} , triclinic $P\bar{1}$, (No. 2), $Z = 4$. Four-circle diffractometer *Siemens P4*, MoK_α radiation. All data corrected for *Lorentz* and polarization effects, $\mu = 0.10$ mm^{-1} , 3248 recorded reflexes within $3^\circ \leq 2\theta \leq 52^\circ$, of which 2948 are independent and 2947 used for refinement ($R_{\text{int}} = 0.0295$). Structure solution with direct methods using *SHELXS-86* [29]. Refinement with *SHELXL-93* [30], 201 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0374 \cdot P)^2 + 0.33P]$, for 2076 $F_o > 4\sigma(F_o)$, $R = 0.0429$, wR^2 for all 2948 reflections = 0.1065, *GOOF* = 1.032, residual density: 0.21/–0.19 $\text{e}/\text{Å}^3$. C, O, and Na centers refined using anisotropic displacement parameters; all H-atoms located from difference-density map, positioned ideally, and refined with isotropic displacement parameters using the riding model ($[U_{\text{iso}} = 1.2 \cdot U_{\text{eq}}(\text{C-H}/\text{CH}_2)]$; $[U_{\text{iso}} = 1.5 \times U_{\text{eq}}(\text{CH}_3)]$). Further details of the crystal-structure determination can be obtained from the *Cambridge Crystallographic Data Centre*.

Comparison of Crystal Densities. For comparison with the data reported [9], the cell constants and the crystal density of our polymorph have been determined in addition at 195 K: $a = 881.9$ (1), $b = 1009.3$ (1), $c = 1060.4$ (1); $\alpha = 102.495$ (5) $^\circ$, $\beta = 106.597$ (5) $^\circ$, $\gamma = 109.364$ (5) $^\circ$, $V = 801.4 \cdot 10^6$ (2) pm³, $d_{\text{calc.}} = 1.211$ g cm⁻³ ([9]: 1.227 cm⁻³). It has to be pointed out, however, that the above structure determination and the one described in [9] have been performed using different diffractometers.

MNDO Calculations. The procedure and all details including the parameter set are specified in [9].

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